

TITLE AND NUMBER		PROJECT AND PROJECT NO.	
<p>Conversion of sugars in the viscose precipitation baths S. N. Danilov, E. V. Zaitsev and L. A. Tsaplina. <i>Org. Chem. Ind. (U.S.S.R.)</i> 2, 395 (1963). Monosaccharides added or formed in the viscose pptn. baths are decomposed by acid with partial conversion into humic substances. The filaments contaminated with the sol and insol. humic substances give unevenly dyed textiles. In spinning without addition of glucose the baths become contaminated with humic substances by the decomposition of glucose, fructose, xylose, etc., formed by hydrolysis of hexosans and pentosans derived from viscose, chiefly from hemicellulose. Glucose is in part converted to fructose. The 2 sugars give humic substance of nearly the same nature. Of the products of their decomposition could be identified oxymethylfurfural, HCO_2H and levulinic acid. Neither $AcOH$ nor furfural was present. Substitution of xylose for glucose in the pptn. baths gave inferior results because of the greater rate of decomposition of the former. Chas. Blanc</p>		<p>Purification of viscose waste lye by oxidation. S. N. Danilov and I. P. Sukhovtova. <i>Org. Chem. Ind. (U.S.S.R.)</i> 2, 648 (1963). Methods of purification and decolorization of spent precipitation liquors by oxidation of the org. impurities with Cl_2 and $NaOCl$ are discussed. About 15 references. Chas. Blanc</p>	
<p>ASS-514 METALLURGICAL LITERATURE CLASSIFICATION</p>			
<p>SEARCHED INDEXED</p>		<p>SERIALIZED FILED</p>	
<p>APR 1964</p>		<p>APR 1964</p>	

Monomerization of acetylene compounds. VI. **Isobutylidene** acid rearrangement of monomers. S. N. Danilov and A. M. Gakhovskaya. *J. Gen. Chem.* (U. S. S. R.) 6, 704-19 (1954); *cf. C. A. 48, 10644*. By analogy with the isomerization of α -Br and α -HO aldehydes into acid, monobasic acids previously studied, monomers substituted in the 1- and 1,2-positions with halogens are capable of the isobutylidene acid type rearrangement. Thus, 2-chlorotrimethylglucoside (I) reacts with $\text{Pb}(\text{OH})_2$ giving directly glucosidic acid (II), called here orthoisobutylidene acid. 2-Chlorotrimethylglucoside (III) gives under these conditions trimethylglucosidic acid (IV). Pentamethylglucoside, m. 120-30°, prep. by heating glucose with Ac_2O and NaOAc , was treated for 3 hrs. with HBr acid. in AcOH at 0°. The reaction product in CHCl_3 was pptd. with petr. ether and recrystd. from AcOH at 0°, giving 70% β -isomer and 30% α -isomer. This (80 g.) in 500 cc. of 50% AcOH was gradually treated, with shaking, with 100 g. Zn dust at 15-25° for 3-3.5 hrs. The filtrate was concd. at 30-5° and 12 mm. pressure and then extd. with Et_2O . After washing the ext. with NaHCO_3 and with Et_2O . off the Et_2O , the drup was allowed to H_2O and distg. off the drup for a few days, giving 53% crystalline in a desiccator for a few days, giving 53% trimethylglucal (V), m. 51-5° (alc.). $[\alpha]_D^{25} -16.4^\circ$ (25% alc.). V, treated with Br in CHCl_3 at 0° and the CHCl_3 distd. off *in vacuo*, gave 90% 1,2-dibromotrimethylglucal, $(\text{OCH}_2\text{Br}, \text{CHBr}, \text{CH}(\text{OAc}))_2, \text{CHCH}_2\text{OAc}$ (VI), $[\alpha]_D^{25} 13.7^\circ$. V with Cl in CHCl_3 gave 66% 1,2-dichlorotri-

acetylglucal (VII), m. 80-92° (Et_2O), $[\alpha]_D^{25} 198.4^\circ$. VI (18 g.) in 100 cc. CHCl_3 shaken with moist Ag_2O (25 g.) gave 2-bromotrimethylglucal, $[\alpha]_D^{25} 60.4^\circ$. VII (20 g.) in CHCl_3 with 30 g. $\text{Ag}_2\text{O} + \text{H}_2\text{O}$ gave 79% I, $[\alpha]_D^{25} 62.5^\circ$ (CHCl_3). The mono- and dibromotrimethylglucosides, treated with $\text{Pb}(\text{OH})_2$, cleave the Ac groups and give II ($\text{HO}-\text{CCH}_2[\text{CH}(\text{OH})]_2\text{CH}_2\text{OH}$). E. g., I (20 g.) in 300 cc. H_2O with 50 g. of freshly prep. $\text{Pb}(\text{OH})_2$ was stirred on a water bath first at 20-5° for 5 hrs. and then at 50°, 60-75° and 85-90° for 25, 25 and 5-10 hrs., resp. The filter cake was dissolved in H_2O and the Pb salt compd. with H_2S . The filtrate was concd. *in vacuo*, the drup didd. with H_2O and again concd. The operation was repeated until all the AcOH was expelled. The drup was digested with an excess of BaCO_3 in H_2O , the filtrate boiled with animal charcoal and the filtrate concd., giving 78% β -glucosidic acid, $[\alpha]_D^{25} 9.4^\circ$. This, decuped. with H_2SO_4 , gave 13.6 g. II, m. 145°, $[\alpha]_D^{25} 4.99^\circ$. The phenylhydrazide of II m. 176°. II, treated with Ac_2O and NaOAc at 70-80° for 10 hrs. and then at 95-100°, gave 3,4,5,6-tetraacetylglucosidic acid, m. 110°; its phenylhydrazide m. 143°. II, treated with MeI in the presence of Ag_2O at 60° for 36 hrs., gave 78% β -3,4,5,6-tetramethylglucosidate (VIII), m. 81.5°, $[\alpha]_D^{25} 84.2^\circ$. VIII, sapcond. with $\text{Ba}(\text{OH})_2$, gave the acid (IX), m. 93-4°; its phenylhydrazide m. 112°. The synthesis of IV from III was studied to show that in the formation of II from the halogen derivs. of V with $\text{Pb}(\text{OH})_2$, no other isomeric anhydric acids are formed. Glucal, m. 80°, $[\alpha]_D^{25} -67.2^\circ$, was prep. by cong. 15 g. V in 100 cc. MeOH with dry NH_3 at 0° and letting it stand at room temp. for 24 hrs. After cong. the mint. *in vacuo*, the drup was distd. at 108° and reduced pressure until it was freed from AcNH_2 . Glucal, digested with a large amount of MeI and AgOAc for 20 hrs., gave 3,4,5-trimethylglucal, $[\alpha]_D^{25} 81.4^\circ$. This (10 g.) in 10 cc. CHCl_3 , treated with Cl at 0° and the CHCl_3 distd. off *in vacuo*, gave 9.1 g. 1,2-dichlorotrimethylglucal, $[\alpha]_D^{25} 121.1^\circ$ (CHCl_3). This in H_2O , CHCl_3 , shaken with moist Ag_2O , gave III. III in H_2O , heated gently with $\text{Pb}(\text{OH})_2$, gave 69% IV; its phenylhydrazide m. 123-5°. IV was converted with EtI into VIII and this into IX.

Hydroxybutylcellulose and its mixed ethers. I. Synthesis and properties of hydroxybutylcellulose. S. S. Danilov and V. A. Kon'kova. *J. Applied Chem.* (U.S.S.R.) 7, 1963 8(1938).—Linter meal was treated with NaOH for 1-2 hrs., pressed to a loss in wt. of 40-60%, and allowed to react with α,β -dimethylethylene oxide in a sealed glass tube or Ag-plated autoclave. The product was extd. from the mother liquor with Et₂O. To remove ash from the product, its alk. soln. was neutralized with 5-10% H₂SO₄ or AcOH, and, after boiling, the ppt. of hydroxybutylcellulose was filtered without allowing it to cool, because it again dissolves on cooling. The temp. of the expts. was 75-80°. A prolonged heating, and an increase of the amt. of dimethylethylene oxide increased the degree of etherification. The synthesis cannot be carried out at room temp., but an increase of the temp. from 80° to 100° had practically no influence. The concn. of alkali is not of great influence. The product is easily sol. in weak NaOH, and difficultly in water. The product contains C 45.94-53.07 and H 6.97-8.05%. Eight literature and twenty-two patent references. II. Hydroxybutylbenzylcellulose. V. A. Kon'kova. *Ibid.* 1969 72.—The half-substituted hydroxybutylcellulose was dissolved (slurpy state) in 30% NaOH and this soln. was treated with C₆H₅CH₂Cl (8 mols. per mol. of cellulose). The product was extd. with alc. and washed with hot water, yielding a white powder contg. 66.7% C, corresponding to a completely substituted product. It is sol. in

1ST AND 2ND SERIES		3RD AND 4TH SERIES	
PROCEDURES AND PROPERTIES INDEX			
<p><i>13C</i></p> <p>Fertilization of carbon, distinguish between cellulosic materials and by-products. S. Denny and S. Ruvy (From. Q. J. Chem., 1947, 2, 688-701).— The relative proportion of CN used for nitrile production and the velocity of formation of Na_2CN inversely as the $[\text{NaOH}]$ of the mixture. Elimination of Na_2CN is observed during the process of nitrilation. Addition of Na_2SO_4 or KCN to the viscous causes a colour change from yellow to red, due to formation of Na_2CN from Na_2CN. Addition of polysulfonates to viscous does not affect the $[\text{Na}_2\text{CN}]$ of the mixture. R. T.</p> <p><i>B-2-5</i></p>			
ASB-114 METALLURGICAL LITERATURE CLASSIFICATION			
FROM SYMBIOSIS		FROM SYMBIOSIS	
SYMBOL NO.		SYMBOL NO.	

23

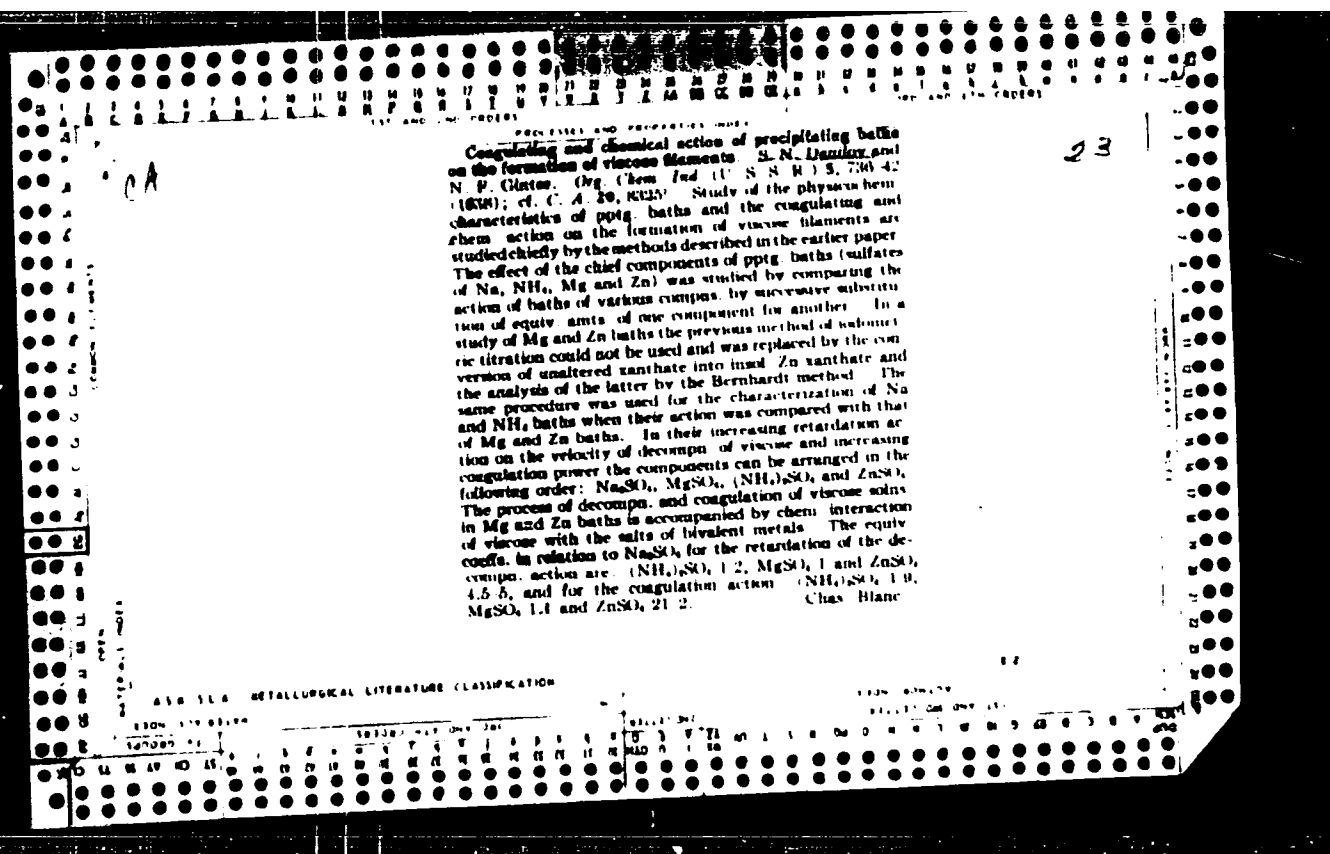
Analysis of viscose. S. N. Denilov and S. M. Risov
J. Applied Chem. (U. S. S. R.) 10, 1045-52 (in French
 1933) (1937).—Free CS_2 in xanthates and in viscose was
 oxid. with cold H_2O_2 and transformed simultaneously into
 Et xanthate, which was detd. by iodometric titration.
 If the viscose contains sulfite and other analogous compounds,
 the iodometric titration cannot be used. In this case the
 analysis was carried out by pptn. of all components of vis-
 cose, yielding insol. salts with Cd and analyzing them by
 the Geiger or the Bernhard method. Analysis of the vis-
 cose by the Fink method was modified. Dipropylchloro-
 acetamide and dimethylchloroacetamide were synthesized
 and used as reagents in the last method. Twenty-three
 references. A. A. Podgorny

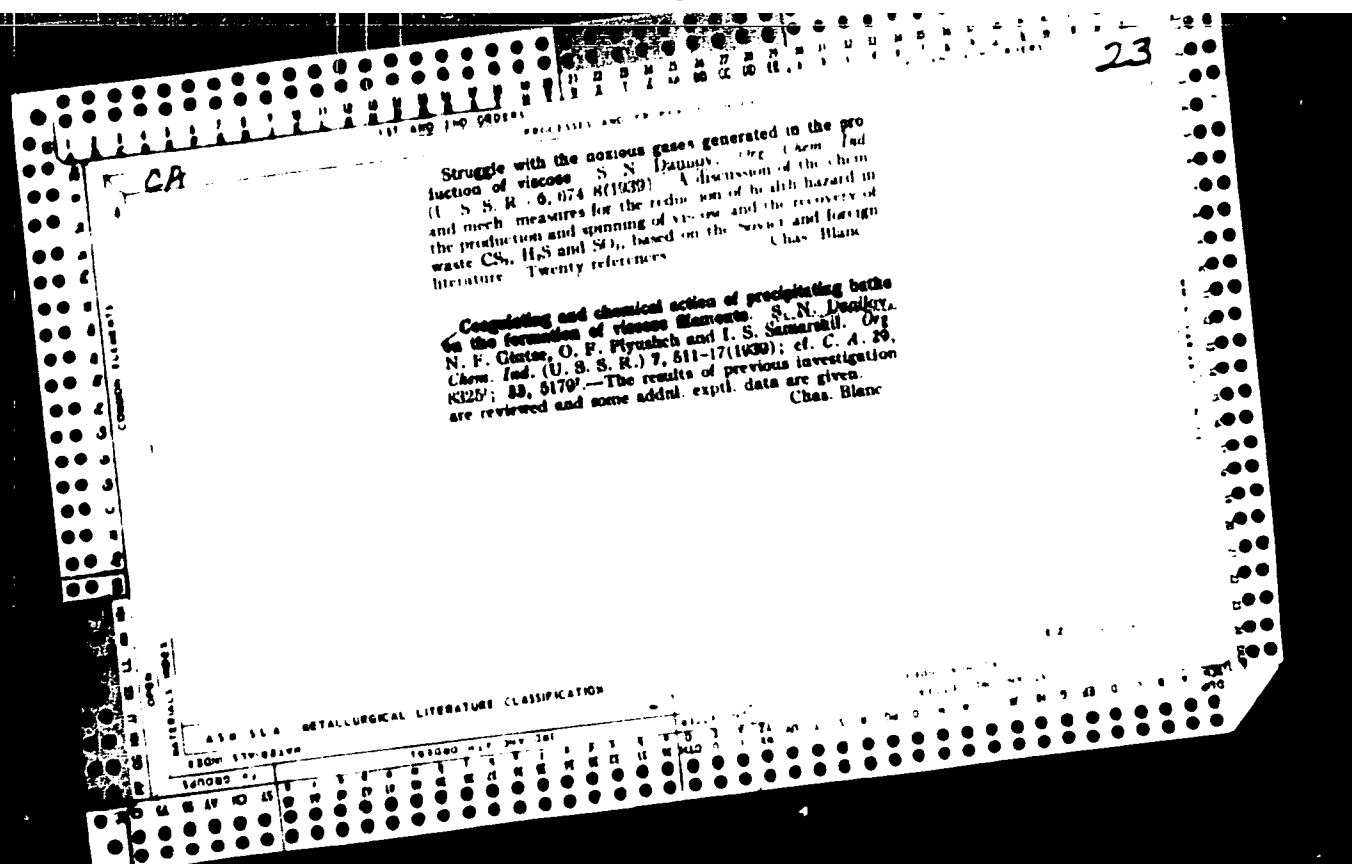
Spinning solutions for cuprammonium rayon. I. Composition and properties of basic copper salts. S. N. Danilov, A. Chernyaeva, N. Goryunova and Yu. Gol'dfarb. *J. Applied Chem.* (U.S.S.R.) 10, 1608, 1614 (in French 1937) (1937). Basic Cu salts I and II were prepd. by fractional pptn. of blue vitriol with soda, and a cryst. hydrated oxide of Cu (III) was prepd. by pptn. of blue vitriol with NH_4OH and then with NaOH . The conditions of prepa. and the compn. of salts affect the degree of dispersion; this perhaps affects the rate of soln. in NH_4OH and also the soly. of cellulose. Salt I contains more SO_4 ion than salt II. The concns. of soda and blue vitriol solns. have practically no effect upon the degree of dispersion and the compn. of basic salts. III is less sol. in NH_4OH in the absence of cellulose, but, having no SO_4 ion, it dissolves cellulose in the NH_4OH soln. better than I or II. The presence of CO_3 ion together with SO_4 ion decreases the soly. of cellulose in the NH_4OH soln. still farther. The analytical methods are described. Thirteen references. II. The influence of salts in the preparation and on the properties of copper-ammonium hydrosulfate solutions of cellulose. S. N. Danilov, Yu. Gol'dfarb, A. Chernyaeva and N. Goryunova. *Ibid.* 1457-67. The influence of electrolytes on the soly. of

basic salts in NH_4OH and the methods for the detn. of maturity of the spinning solns. were investigated. III dissolves better in the NH_4OH soln. in the presence of Na_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$, but the soly. of cellulose in the NH_4OH soln. of III is lowered in the presence of much $(\text{NH}_4)_2\text{SO}_4$. Small quantities of Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ affect the soly. of cellulose and basic salts (in the presence of cellulose) but slightly. Salt II dissolves cellulose to a smaller extent in the presence of $(\text{NH}_4)_2\text{SO}_4$, but itself dissolves better in the presence of electrolytes and cellulose. The coagulating action of the strong alkali decreases according to the series $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The NH_4 salts have the greatest coagulation action. In this case the anion is of importance, thus the following lyotropic series was established: $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{CNS}^- > \text{HCO}_3^-$. The amts. of salts which should be used for coagulation depend upon the compn. of the Schweitzer solns. Four references. III. The role of organic admixtures in the spinning copper ammonium hydrosulfate solutions. S. N. Danilov, D. Brokhina and E. Maryanova. *Ibid.* 1615-23 (in French 1937). Addn. of glucose has no effect upon the soly. of basic Cu salts (in the presence of cellulose) and upon the soly. of cellulose. Addn. of glucose to the copper NH_4OH solns. of cellulose increases the viscosity of the solns. by several times, and

added in larger amts. (above 20% by wt. of cellulose) causes pptn. of cellulose. Increase of acid, I and Cu nos. on passing air or O (with precautions against loss of NH_3) through the solns. contg. no glucose is greater than in solns. containing glucose. Thirteen references. I.A.P.

ASH-542 METALLURGICAL LITERATURE CLASSIFICATION





Glycerol derivatives of cellulose S. N. Danilov, M. E. Dvorkin, N. I. Orlovskaya and A. A. Rafailukov. *J. Gen. Chem.* (U. S. S. R.) 9, 10, 481 (1969). An attempt was made to prep. water-sol. glyceryl ethers of cellulose from alkali cellulose and glycerine monochlorohydrin (I), dichlorohydrin (II), and glycidol (III). Alkali cellulose was prepd. by the action of 30% NaOH soln. on linters contg. cellulose 95% moisture, 3.8% ClO₂, ash 0.25 and 1.0% alkali (0.15%). In attempts at etherification in py-

ridine, there was no reaction at low temp., and tarring occurred at higher temp. Direct action of I on alkali cellulose was difficult, owing to poor wetting. Glycerol ethers were formed when 8 mols. of I was used per mol. of Cell_{alk}. The resulting ethers retained the fiber structure. The soly. of the ethers is adversely affected by small amounts of dichlorohydrin in I. Alkali cellulose treated with 8 mols. of II in boiling acetone for 24 hrs., poured in water, neutralized with acetic acid and dried with dry air at 50° gave ethers insol. in org. solvents, but swelling in formic acid. Glycerol residue per Cell_{alk} was 1.2. Alkali cellulose heated for 24 hrs. in an acetone soln. of III, in the ratios III:Cell_{alk}, 2:1, 4:1, 6:1, 8:1 each for 24 hrs., 10:1 for 30 hrs. and 8:1 for 48 hrs. gave ethers contg., resp., glycerol residue per Cell_{alk}, 0.12, 0.25, 0.41, 0.64, 1.01, 1.86 with the water solubilities 1.7, 2.9, 6.3, 8.9, 12.3 and 39.9%. Nitration and acetylation of the ethers showed those from III contained more OH groups than those from II. The nitrated products were soluble in acetone; insol. in alc-ether mixts. Ethers prepd. from II contained no Cl. D. Arlony.

Lab. of Leningrad
Chemico-Tech. Inst.

1ST AND 2ND COPIES		PROCESSING AND PROPERTIES INDEX		3RD AND 4TH COPIES													
122				13-II-5													
<p>Influence of inorganic salts on properties of cellulose acetate solutions. S. N. DAVILOV, J. M. GONCHAROV, and E. V. KARVINA (J. Appl. Chem. Russ. 1939, 12, 83-84).—Inorg. salts (Ca, Mg, and Na salts present in H₂O) and Fe salts originating from corrosion of apparatus) cause turbidity, coagulation, and emulsions of an. C₂H₅CO₂ solutions of cellulose acetate (I). Salt-free (II) is prepared by fractional pptn. from C₂H₅CO₂ by Et₂O. (I) bleached with KMnO₄ contains traces of MnO₂; the use of salt-free bleaching agents, such as H₂O₂, is recommended. R. T.</p>																	
<p>W. A. Gelshteyn, S. N. Davilov, J. Applied Chem. (U. S. S. R.) 13, 1033-33 (1939).—An obituary with a portrait. A. A. Podgorny</p>																	
ADD-51A METALLURGICAL LITERATURE CLASSIFICATION																	
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CA		<p>In memory of Pavel Polakhtovich Sharygin. S. N. Danilov. <i>J. Gen. Chem. (U. S. S. R.)</i> 10, 176-82 (1940). Obituary, with portrait and bibliography and summary of his researches and activities. Chas. Riazor</p> <p>The eightieth year of A. E. Favorskii. A survey of his fifty-five years of scientific and teaching activity. S. N. Danilov. <i>J. Gen. Chem. (U. S. S. R.)</i> 10, 387-401 (1940). —A review of F.'s work with portrait and bibliography. H. M. Leicester</p>		2	
<p>Lab. of Organic Chem., Scientific-Res. Chemical Inst. of the Leningrad State University.</p>					
<p>ASB-ILA METALLURGICAL LITERATURE CLASSIFICATION</p>					
1ST EDITION		2ND EDITION		3RD EDITION	
1ST EDITION		2ND EDITION		3RD EDITION	

PROCEDURES AND PROPERTIES INDEX										100 AND 210 COVER									
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1A

The relation of nitrocelluloses of differing degree of heterogeneity to volatile and nonvolatile solvents

Danilov, *Izvestiya Akad. Nauk SSSR Khim. Nauk*, 1941, No. 1, p. 104. (Eng. transl. in *Proc. Acad. Sci. USSR Div. Chem. Sci. Engl. transl.*, 1941, No. 1, p. 104.)

Fractionation of nitrocellulose from Me₂CO and Et₂O followed by pptn. with H₂O, sep. apparently homogenous fractions into fractions with different N₂ content. The more acid fractions have no peptizing action on the solvent. Fractions contg. about 12% N₂ show greatly reduced rapid absorption of solvent vapor. Swelling pressure of the fractions after absorption of solvent depends on degree of nitration and temp. but not on viscosity of the solns. Fractions which swell most have lowest viscosities in soln. and form more porous gels.

H. M. Eichen

Analysis in production of cellulose esters R. N.
Pankov, *Trudy Vsesoyuz. Nauchnoiss. Inst. Khim.
Akad. Nauk S. S. S. R.* 3, 204 (1944). Review of
general analytical methods used in cellulose ester produc-
tion: Ca number, oxycellulose, polymer detn. in viscose,
analysis of nitration mixt. and detn. of total org. matter
9 references G. M. Kosolapoff

DANILOV, S. N. ✓

Reaction of cellulose nitrate with solvents. S. N. Danilov and V. P. Danilin (*J. Gen. Chem. Russ.*, 1945, 16, 550-564).—The swelling pressures developed during imbibition of org. solvents (COMe₂ and EtOH-Et₂O) by various specimens of cellulose nitrate have been measured by means of the special apparatus described; the velocity of imbibition is expressed by $K = (2.3/t) \log (P_{\infty} - P_0)/(P_{\infty} - P_t)$, where P_{∞} is the limiting swelling pressure, and P_t and P_0 are the pressures at times t and 1 hr. respectively. The work performed during swelling falls with rising N content, but

is independent of the mol. wt. of the specimens. Successive extractions of cellulose nitrate containing 12.5% N, by means of COMe₂-Et₂O mixtures of increasing COMe₂ content, give a series of fractions of diminishing N content from 12.62 to 11.40%, while with an original N content of 13.10%, that of the fractions rises from 11.94 to 13.19%. It is concluded that the most reactive fraction is that containing 12-12.5% N. The η of a solution of cellulose nitrates of various N contents is \propto would follow from the addition rule.

Lab., Cellulose, Leningrad Chemico-Technological Inst. im. Lensovet.

DANILOV, S.N.

Characteristics of modern organic chemistry and the role of the
Butlerov-Favorskii School in its development. Vest. Len. un. 2
no.1:103-126 Ja '47. (MLRA 9:6)

1.Chlen-korrespondent AN SSSR.
(Chemistry, Organic)(Butlerov, Aleksandr Mikhailovich, 1828-1886)
(Favorskii, Aleksei Evgrafovich, 1860-1945)

FA 15T78

DANILOV, S. N.

USSR/Chemistry - Viscose
Viscose

Mar 1947

"Softening of Viscose (Cellophane) Films with
Glycerine Water Solutions," S. N. Danilov, M. A.
Sokolovsky, A. I. Evdokimova, 15 pp

"Zhur Obshch Khim" Vol XVII, No 3

It was found that the degree of swelling of the films
in water solutions was considerably higher than in
water alone, and that the constituents of the
softening bath were absorbed by the films in
proportions differing from those in which they are
present in the bath.

15T78

C3f.R
E4.R

PAKHOV, B. N.

Corresponding member of AN SSSR

Delivered a paper "Gomogenyy kataliz pri oksiditel'no-
vechatno-vitel'nykh prevrashcheniyakh organicheskikh
soyedineniy", at Vses. konferentsiya po katalizu,
May 1947, Moscow.

Source: Uspekhi Khimii, 1947, No. 4, p. 502

1-1

R4D.R
C3.R

PAVLOV, S. N.

Delivered a paper "Nabukhaniye tsellyulozy v mineral'nykh
kislotakh i svoystva gidrotsellyulozy" at Chetvertay konferen-
tsiya po vysokomolekulyarnym soyedineniyam, May, 1946

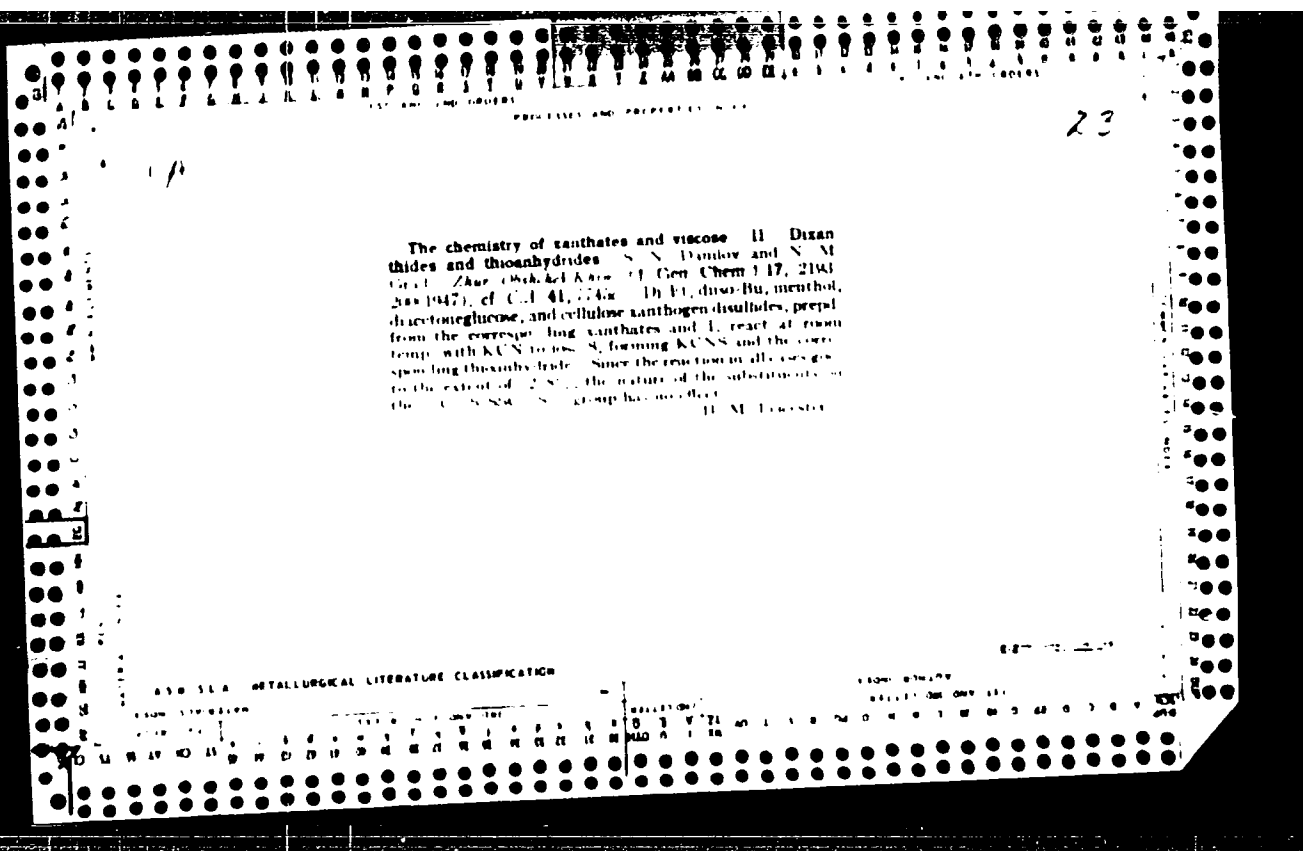
Khimicheskaya Promyshl. 1946, No. 7-8, p. 17

1-1

Mixed cellulose ethers. 1. Reaction mechanism for the acetylation of nitrocellulose with acetic acid and the production of nitroacetylcellulose. S. N. Danilov, M. A. Sokolovskii, and A. I. Bydokimova. *Zhur. Obshch. Khim.* (J. Gen. Chem.) 17, 1888-93(1947).—Nitrocellulose was treated with 5 parts glacial AcOH and 0.15 part H_2SO_4 ; during 120 hrs. at 20° the N content fell from 11.63 to 8.63%, while the Ac content rose to 7.94%. During 96 hrs. at 30° the N content fell from 11.62 to 1.92%, while the Ac content rose to 43.63%. On a molar basis the entering Ac groups just balance the displaced NO_2 groups. The solubilities of intermediate nitroacetylcelluloses in various org. solvents is given qualitatively. I. P. Danchev

Molecular rearrangements of organic compounds according to the work of chemists of the U.S.S.R. during the 1917-1947 period. S. N. Danilov. *J. Gen. Chem.* (U.S.S.R.) 17, 1925-80(1947).—Review with 232 references. G. M. Kosolapoff

Academician A. E. Arbuzov—head of the Kazan school of organic chemists. S. N. Danilov. *J. Gen. Chem.* (U.S.S.R.) 17, 2117-28(1947)(in Russian).—Review of scientific work with bibliography and portrait. G. M. Kosolapoff



DANILOV, G. G.

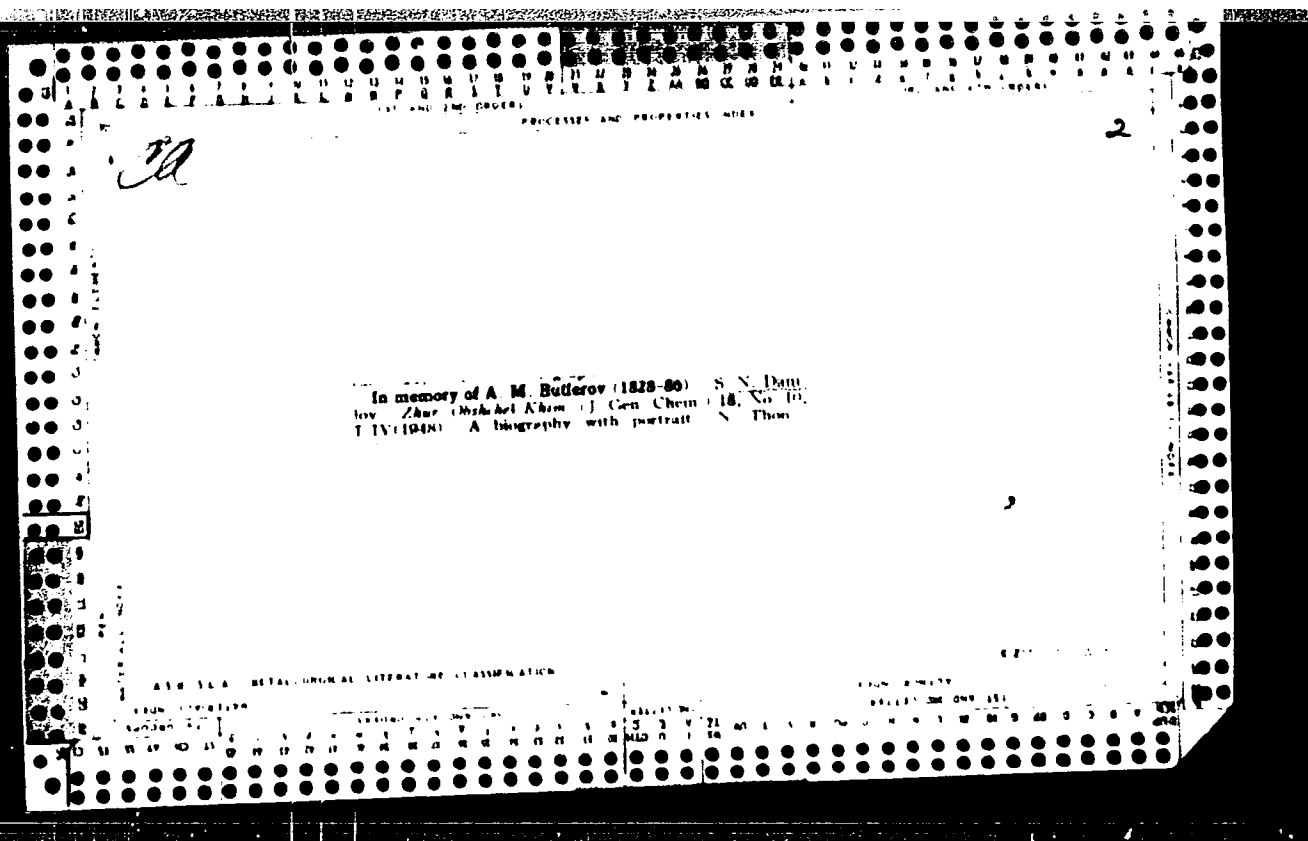
Danilov, G. G. "Is the Soviet Union a superpower?"
Kievskaya pravda, 1986, 10 July, p. 1. (Soviet Union)
Sov. author(s), Moscow, 1986, 10 July, p. 1.

CC: "Soviet Union," 10 July 1986, 10 July 1986, 10 July 1986.

DANILOV, S. N.

"Danilov, S. N. "Effect of mineral acid on cellulose and behavior of hydrocellulose,"
in symposium: Issledovaniya v oblasti tsellyulozy i yeye sputnikov, Moscow-Leningrad,
1948, p. 88-97 - Bibliog: p. 97

SO: U-2888, Letopis Zhurnal'Statey, No. 1, 1949



USSR/Chemistry - Polymerization
Cellulose

Oct 48

2,54155
"The Three-Dimensional Structures of Molecules:
II, The Oxidation-Polymerization of Allylcellulose
(I)," S. N. Danilov, O. P. Koz'mina, Lab of State
U. of Applied Chem, 9 1/2 pp

"Zhur Obshch Khim" Vol XVIII, No 10

Under effect of heat and light, oxygen unites with I
and subsequent decomposition of the oxidized molecule
according to position of double bond occurs with
cleavage of formaldehyde and formation of three-
dimensional structures by means of combination of
USSR/Chemistry - Polymerization Oct 48
Cellulose (Contd)

ether-cellulose chain links. Oxidation-polymeri-
zation occurs not only from activity of free
oxygen but as a result of combined oxygen. No
polymerization occurs in absence of oxygen. Dur-
ing chlorination of I which proceeds according to
the presence of available double bonds, a quantita-
tive yield of chloro-substituted allyl ether of
cellulose is produced, which readily passes over
with cleavage of HCl into unsaturated chloro-com-
pounds. Subsequently, the latter are quickly
polymerized with formation of a chlorine-contain-
ing polymer of chloroprene type. Submitted
1 Oct 47.

DANILOV, S. N.

PA 67/49T19

USSR/Chemistry - Isomerization
Aldehydes

Nov 48

"Hydro- and Solvolytic and Intramolecular Oxidation-Reduction: II, Acid and Acid-Salt Catalysts During Isomerization of Aldehydes in Ketones," S. N. Danilov, Lab Imeni A. Ye. Pavlovskiy, Leningrad State U, 8 pp

"Zhur Obshch Khim" Vol XVIII, No 11

Isomeric transformation of aldehydes to ketones is a catalytic reaction which occurs under conditions of homogeneous, quasi-homogeneous and heterogeneous catalysts, depending on the properties of the

67/49T19

USSR/Chemistry - Isomerization (Contd) Nov 48

compounds and the catalyst. Studied isomeric transformation of aldehydes to ketones in the presence of H_2SO_4 and mercury. Submitted 15 Sep 47.

67/49T19

DANILOV, S. N.

PA 67/49T22

USSE/Chemistry - Isomerization
Aldehydes

Nov 48

"Isomerization of Oxyaldehydes: XII, Oxyketones With
a Primary Alcoholic Group and Their Relation to
Alpha-Oxyaldehydes and to Isomeric Alpha-Oxyketones,"
S. N. Danilov, N. S. Tikhomirova, Lab imeni A. Ye.
Favorskiy, Sci Res Chem Inst Affiliated With Lenin-
grad State U, 7 pp

"Zhur: Obshch Khim" Vol XVIII, No 11

Found that 1-chloro-2-butanol was converted either
to hydroxymethyl ethyl ketone or 2-methyl-alpha-
hydroxyethyl ketone, depending on the conditions of
the reaction. Submitted 15 Apr 48.

67/49T22

DANILOV, S.N.

4

9 // Homogeneous catalysis and the oxidation-reduction conversion of organic substances. S. N. Danilov. *Problems of Kinetics and Catalysis, Abstr. No. 5-9, 1949, 309-10 (1949).*—The intermol. and intramol. oxidation-reduction of org. substances in the presence of homogeneous catalysts (acids, bases, org. bases, metal salts) are discussed. The mechanisms for these reactions are discussed and it is shown that the mechanism depends on the extl. conditions. J. Rovtar Leach

MA
gen

DAVIDSON, S. N.

PA 46/49T17

USSR/Chemistry - Amines
Chemistry - Chlorination

Feb 49

"Interaction of N-Cl Amines With Other Amines,"
S. N. Davilov, O. P. Koz'mina, 9 pp

"Zhur Obshch Khim" Vol XIX, No 2

Establishes that in primary and secondary aromatic amines, and in aliphatic aromatic amines, nitrogen atom of which is directly bonded with benzene ring (dimethylaniline, chlorination of ring (C-chlorination) occurs under action of chloramines. Primary amines are completely replaced by chlorine while excess chloramine is

46/49T17

USSR/Chemistry - Amines (Contd.)

Feb 49

oxidized into azo compounds. In primary and secondary aliphatic and aliphatic aromatic amines, nitrogen of which is bonded with aliphatic ring, and not with aromatic ring (benzylamines), chloramines enter reaction of double decomposition (N-chlorination). Action of chloramines on tertiary aliphatic amines and on tribenzylamine results in cleavage of one alkyl group with oxidation of it into the aldehyde group and chlorination (in nitrogen) of the dialkylchloramine forming. Submitted 20 Nov 47.

46/49T17

DANILOV, S. N.

PA 67/49T58

USBR/Chemistry - Oxidation
Cellulose

May 49

"The Chemistry of Viscose and Xanthogenates: III,
Oxidation Reactions in Alkalicellulose and Viscose,"
S. N. Danilov, N. M. Grad, Ye. I. Geyne, Lab of
Chem Processing of Cellulose, Leningrad Technol
Inst Imeni Lensovet, 17 pp

"Zhur Obschch Khim" Vol XIX, No 5

Study of the oxidation of alkalicellulose in the
presence of retarding and accelerating impurities
showed that sodium sulfite alone or with sodium sul-
fide markedly retarded the activity while the sulfide

67/49T58

USBR/Chemistry - Oxidation (Contd)

May 49

alone produced a less marked effect. Retardation
in this case was actually preceded by an acceleration
in the first moment of the reaction. Noted similar
retarding effects for sodium sulfite and sodium sul-
fide in viscose. Demonstrated that the xanthogenates
of ethyl alcohol, diacetone glucose, and cellulose
react with oxygen to form dixanthogenides. Sub-
mitted 18 Jan 48.

67/49T58

USNR/Chemistry - Viscose
Oxidation - Reduction

"The Chemistry of Xanthogenates and Viscose. IV. Viscose Components Which Add and Split Off a Sulfur Atom: Oxidative and Reductive Sulfur Addition,"
S. B. Danilov, N. M. Grad, A. F. Vorob'yeva, Lab of Chem Reprocessing of Cellulose, Leningrad Tech Inst
Leningrad, 321 pp

"Zhur Obshch Khim" Vol XIX, No 7

Describes composition of viscose, and considers addition and cleavage of sulfur by viscose components. Conducted experiments on secondary sulfur-containing substances, on relation of viscose components to

USGR/Chemistry - Viscose
Oxidation - Reduction

sulfur-cleaving substances, and on interaction of sulfur-cleaving substances and sodium disulfide. Made quantitative determination of the amount of labile sulfur in viscose. Submitted 20 Mar 48.

2/50169

DANILOV, S. N.

62/49T22

USSR/Chemistry - Xanthogenates

Jun 49

The Chemistry of Viscose Xanthogenates:

V, Thioanhydrides of Xanthogenic Acids and Their Conversion," S. N. Danilov, N. M. Grad, V. O. Klesman, Lab for Chem Processing of Cellulose, Leningrad Technol Inst (ment Leningrad, 8 1/4 pp

"Zhur Prikl Khim" Vol XIII, No 6

Shows that chemical properties of monoxanthogen-sulfides or the thioanhydrides of xanthogenic acids are similar to those of xanthogenalsulfides or dioxanthogenides. In a water solution, an alkali on thioanhydrides of celulosoxanthogenic

62/49T22

USSR/Chemistry - Xanthogenates (Contd) Jun 49

acid yields cellulose xanthogenate with a carbon oxyanhydride by-product, and using an aqueous ammonia solution, cellulose ammonium xanthogenanhydride with a hydrogen sulfide by-product. Thioanhydrides cannot exist in viscose solutions with a general alkalinity of about 7%.

62/49T22

CA

Characteristic lines of development of chemistry in
U.S.S.R. during the years of Stalin five-year plans. S. N.
Danilov. Zhur. Obshch. Khim. 1) Gen. Chem. 20.
5-30 (1954). — Review with many references, largely con-
cerned with petroleum, hydrocarbon, and cellulose chemis-
try, although protein chemistry is also briefly outlined.
G. M. Kosolapoff

The molecular rearrangements of organic compounds in
the light of Butlerov's structural theory. S. N. Danilov.
Gen. Chem. U.S.S.R. 20, 2307, 2410 (1954) Engl. trans-
lation. See C.A. 45, 6565.

CA

10

Anhydrides of amino and guanidino derivatives of carbohydrates and polyatomic alcohols. 1. 6-Amino, 6-dimethylamino, and 6-guanidino derivatives of glucosyl-
anose. S. N. Danilov and I. S. Libanskii. *Zhur Obshch. Khim.* (J. Gen. Chem.) 21, 366-74 (1951).—Vigorous stirring of glucose and MeCO (1:20 ratio) with 5% by wt.

of H₂SO₄ (1:10) followed by stirring with NaCO₃ (2:10) anhyd. salt (100 g. H₂SO₄), letting the mixt. stand 12-24 hrs., filtration, and evapn. in vacuo yields 65% *diacetonoglucose*, m. 111-12° (from petr. ether). This in 8 parts EtOAc is treated with HNO₃ (d. 1.3) (1 ml. 100 ml. soln.) and heated on a steam bath 5 min., yielding 70% *monoacetonoglucose*, m. 161-2°, hydrolysis in 50% MeOH and H₂SO₄ at room temp. is more laborious. Treatment with 1 mole p-MeC₆H₄SO₂Cl in CHCl₃-pyridine and washing with H₂O gives 55% of the 6-*tosyl deriv.*, m. 106-7°. This is cooled to -20° in dry CHCl₃ and immediately upon initial crystn. is treated with 1 mole MeONa in dry MeOH and shaken 25 min., giving after treatment with cold H₂O 85% 1,2-*isopropylidene-3,6-anhydroglucosyluramine*, m. 131-4° (from C₆H₆). Heating this with 8% dry NH₃ in dry MeOH 2 hrs. to 80°, after an initial 3 hrs. at 20°, and evapn. in vacuo gave 85% of probably 1,2-*isopropylidene-6-deoxy-6-aminoglucose*, m. 60-5°, a very hygroscopic substance, yielding a carbonate

(C₁₂H₂₀N₂O₅·H₂CO₃) m. 90-5° from EtOAc. Similarly MeNH₂ in dry MeOH gave a simple yielding carbonate (C₁₂H₂₀N₂O₅·H₂CO₃) apparently the N,N-dimethyl analog of the above. Several attempts to bring about reaction of guanidine with the anhydride failed, yielding neutral N-free products. Addn. of 40 g. MeI to 20 g. thiourea in 20 ml. dry MeOH and heating 0.5 hr. at 40° gave N-methyl-methylthiourea HCl m. 117°. This added to the 6-amino deriv. (above) in H₂O at 80° gave after 6 days, and treatment with H₂Cl in pyridine, the *triacetonate of monoisopropylidene-guanidinoglucose*, with acyl groups on the 3 and 6 positions, the product, m. 88-91° (from Me₂CO). When 1 day are consumed in the benzoylation. A 4-hr. reaction of 4 g. 6-amino deriv. and 4 g. thiourea deriv. from Me₂CO soln. followed by evapn., thorough drying from Me₂CO soln. and treatment with Ag₂O, gave a hygroscopic 1,2-*isopropylidene-6-deoxy-6-guanidinoglucosyluramine*, m. 110-15° (sealed tube); *picrate*, m. 148-9° (from dil. EtOH). If H₂NCN·NHOMe is used in the prepn., the same product is obtained. The reagent is best prepd. by triturating red Hg oxide under H₂O to yield cyanamide, which is isolated by vacuum drying, is treated with dry MeOH contg. 1 mole dry HCl and is cooled, after standing overnight, the HCl salt of O-methylthiourea crystallizes on chilling, the free base forms by addn. of MeONa to the salt in abs. MeOH. G. M. K.

1451

USSR/Chemistry - Structural Theory Oct 51

"A. M. Butlerov, Founder of the Theory of Chemical Structure," S. N. Danilov

"Zhur Obshch Khim" Vol XXI, No 10, pp 1733-1748

Reviews Butlerov's activity which, although mainly historical, reflects the current controversy on the subject of resonance and org structural theory in general. Author Danilov states that Butlerov, who discovered tautomerism, regarded it correctly as equil isomerism and did not assume oscillation of the hydrogen atom. According to Danilov,

194721

USSR/Chemistry - Structural Theory Oct 51
(Contd)

many of Butlerov's discoveries, neglected under tautism, are now being applied in connection with USSR industrial developments.

194721

DANILOV, G. N.

Chemical Reactions

Consecutiveness in the course of chemical reactions in the case of intermediate compounds during isomeric conversions. Vestn. Leningr. univ., No. 12, 1952.

9. Monthly List of Russian Accessions. Library of Congress, _____ 1953, Uncl.

DANILOV, S. N.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

CATALYSTS

② full
Compounds containing a three-membered oxirane ring.
Reaction of ethyl ester of β,β' -dimethylglutamic acid with
ammonia. S. N. Danilov and V. P. Markovskii. Zh. Org.
Khim. (U.S.S.R.) 28, 1818-21 (1953) (Engl. translation).
See C.A. 47, 8016a.

H. L. H.

8-30-54
JHP

Item (3)

[illegible]

Refluxing IV 1 hr. with MeOH and crushed marble, and letting stand overnight gave 61% 2-methyl-2-methoxy-1-butanone oxime (VII), n_D^{20} 1.80-90°, and some V. Similarly, EtOH gave the 2-EtO analog, b_p 84-85°, n_D^{20} 1.4165. Refluxing IV in Et₂O with dry KOAc 4.5 hr. gave 2-methyl-2-acetoxy-1-butanone oxime, m 102-3° (from ligroine). IV (16 g.) refluxed in Et₂O with 20 g. NaHCO₃ 6.3 hrs. gave 55.5% 2-methyl-1-buten-3-one oxime, (VD) b_p 65-7°, n_D^{20} 1.43-4°, a mixt. of marble and NaHCO₃ gave the same product, b_p 68°, which solidifies on standing (m 43-4°), and a liquid portion, d_{16} 0.9529, n_D^{20} 1.4833, an isomer of the above; on long standing it is transformed to the above solid form. Addn. of 2.4 g. IV in Et₂O to 15 g. SnCl₄ in Et₂O satd. with HCl with cooling gave 2-methyl-3-aminobutane. HCl, m 210°. On hydrogenation of VI over Raney Ni in EtOH VI took up somewhat over 2 mols. and gave 2-methyl-3-aminobutane, b_{100} 85-8.5°, n_D^{20} 1.4060, whose HCl salt m 210°; the yield was very low if the solid isomer of VI was used and some 40% from the liquid isomer; pure 2-methyl-3-aminobutane, b_{100} 85-8.5°, d_{16} 0.7478, n_D^{20} 1.4047. The same amine is formed on hydrogenation of Me₃HC(C=NOH)Me over Raney Ni in EtOH. Similar reduction of VII gave 2-methyl-2-methoxy-3-aminobutane, b_{100} 133-3.5°, while V gave 45% 2-methyl-3-amino-2-butanol, (VIII) b_{100} 156-0°, d_{16} 0.9260, n_D^{20} 1.4497, with abs. EtOH the yield rises to 70% of crude amine; along with this is formed an unstated yield of (Me₃C(OH)CHMe)₂NH, m about 30°, b_{100} 252-4°. 2-Methyl-1-butanol-3-oxime, b_{100} 134.5°, m 42-4°, hydrogenated in abs. EtOH gave 52.3% crude 2-methyl-3-amino-1-butanol (IX), b_{100} 194°, d_{16} 0.9389, n_D^{20} 1.4578. VIII (6.1 g.) in 10 ml. H₂O treated with 6 ml. concd. H₂SO₄, and 10 ml. H₂O and distd. over 2 hrs. at bath temp. 143°; then treated with NaOH, gave 1.7 g. 2-methyl-3-amino-1-hulene, b_{100} 88.9°, d_{16} 0.7745, n_D^{20} 1.424. HCl salt, m 153-3.5°; picrate, m 171°. Pure amine

butene, $b_{\text{m}} 87.5-9.5^\circ$, $d_{\text{m}} 0.7784$, $n_D^{20} 1.4265$, $d_{20} 4.7752$, $n_D^{25} 1.4120$. Similar polymerization of IX gave a trace of product, $b_{\text{m}} 87.5-9.5^\circ$, $d_{\text{m}} 0.7784$, $n_D^{20} 1.4305$. II. Reaction with isobutylene. K. A. Grogan (Ibid. 2121-6—Acid-catalyzed polymerization of isobutylene at -13°) and letting the mixture stand overnight at -20° gave, from 41 g. NOCl and 30 g. of isobutylene, colorless crystals, $b_{\text{m}} 103-4^\circ$ (from pet. ether), $b_{\text{m}} 103-4^\circ$ (from CH_2Cl_2), $d_{\text{m}} 0.8770$, which after distillation gave a colorless liquid, $b_{\text{m}} 82-3^\circ$, identified as 1-amino-2-nitroso-2-methyl-2-butanol. II. Hydrogenation of II over Raney Ni in EtOH gave 1-amino-2-methyl-2-butanol, $b_{\text{m}} 83-5^\circ$, $d_{\text{m}} 0.8770$, isolated as the di-HCl salt, $b_{\text{m}} 103-4^\circ$. IX. Hydrogenation of IX over Raney Ni, dimer of the oxime of 1-amino-2-methyl-2-butanol. Heating 1.45 g. with 180 ml. H_2O and 10 g. of Raney nickel gave much CO_2 and yielded 64% of 1-amino-2-methyl-2-butanol. III. $b_{\text{m}} 83-5^\circ$, $d_{\text{m}} 1.0675$, $n_D^{20} 1.4265$, $n_D^{25} 1.4095$. A similar reaction in MeOH gave 1-amino-2-methyl-2-butanol, $b_{\text{m}} 83-5^\circ$, $d_{\text{m}} 0.8770$ (from pet. ether), while EtOH gave the EtO analog, $b_{\text{m}} 64-5-5^\circ$, $d_{\text{m}} 0.8840$, $n_D^{20} 1.4161$, $n_D^{25} 1.4023$, and PqOH 30.5% crude EtO analog, $b_{\text{m}} 83-5^\circ$, $d_{\text{m}} 1.0439$, $n_D^{20} 1.4420$, $n_D^{25} 1.4414$. Heating I, $b_{\text{m}} 83-5^\circ$ with KOAc and AcOH, then 1 hr. at $80-85^\circ$, gave 2,3-diamino-2-methyl-2-butanol, 53%, $b_{\text{m}} 97-2^\circ$, $d_{\text{m}} 0.8900$, $n_D^{20} 1.4661$, $n_D^{25} 1.4501$. Hydrogenation of the alkoxyl form, above over Raney Ni in EtOH gave 1-amino-2-methyl-2-methyl-2-butanol, $b_{\text{m}} 88-2^\circ$, $d_{\text{m}} 1.0155$, $n_D^{20} 1.4525$, $n_D^{25} 1.4400$. IV. Oil, $b_{\text{m}} 122-3^\circ$, $d_{\text{m}} 1.0243$, $n_D^{20} 1.4600$, $n_D^{25} 1.4430$. V. Oil, $b_{\text{m}} 132-3^\circ$, $d_{\text{m}} 0.8667$, $n_D^{20} 1.4180$ (50%); 1-amino-2-methyl-2-propanol, $b_{\text{m}} 140-50^\circ$, $d_{\text{m}} 0.9323$, $n_D^{20} 1.4400$ (another specimen, $b_{\text{m}} 150-50^\circ$, $d_{\text{m}} 0.9294$, $n_D^{20} 1.4278$, $n_D^{25} 1.4452$, was obtained in 53% yield by hydrogenation of III in EtOH over Raney Ni at 100° and 80 atm. II. Dehydration of this gave H_2SeO_4 (L. Adams and J. H. Jones, J. 43). Nitrosation gave α -nitro-1-amino-2-methyl-2-butanol, $b_{\text{m}} 92-3^\circ$, $d_{\text{m}} 0.9100$, $n_D^{20} 1.4350$, $n_D^{25} 1.4200$. VI. Oil, $b_{\text{m}} 77-9^\circ$, $d_{\text{m}} 0.8782$. The colorless oil repeated distillation gave $b_{\text{m}} 77-9^\circ$, $d_{\text{m}} 0.8782$, $n_D^{20} 1.4280$, $n_D^{25} 1.4130$, $d_{20} 4.7752$, identified by mass spectroscopy as 1-amino-2-methyl-2-butanol. M. K. S. reported by

7-13-59

DANILOV, S. N.

CZECH

Anhydrides and chlorohydrins of xylitol and sorbitol.
S. N. Danilov and V. B. Kazimirova (Leninist Technol.
Lab., Moscow), Zhurnik. State Obshchest. N. in. 2,
1970-50(1953); cf. C.A. 46, 1956. Xylitol (m. 93-94°),
treated in molten state with dry HCl at 100° (1.5 g. per 10
g.) gave a syrup, which after prolonged drying over KOH
was distd., yielding 2 g. O.CH₂.CH(OH).CH(OH).CHCH₂Cl
(l), b. 100-101°. I also formed on heating xylitol 20 hrs. at
106-8° with 10 parts concd. HCl in a sealed tube; the
product, b. 162-5°, d₄ 1.3802, n_D 1.4989 slowly crystd.
and m. 43-5°; pure product, m. 44-5° (from EtOAc).
Passage of dry HCl into "1,4-xylitane" similarly gave 51%
I; dissolvable, from H₂Cl and pyridine at 0°, m. 114-15°
(from EtOH). I heated in dry Me₂CO with dry NaOH 10
hrs. at reflux gave 60% 1,4:2,6-dianhydroxylitol, C₆H₈O₄
b. 113-15°, d₄ 1.2500, n_D 1.4725; the product also forms in
42% yield on treatment of I in Me₂CO with MeONa 48 hrs.
at room temp. Treatment of 20 g. sorbitol with dry HCl

CZECH

S. N. DAVILEV

in AcOH 8 hrs. at 130-40°, until a 2.7-g. gela is reached, gave a syrup, which treated with dry NaHCO₃ in abs. EtOH gave 1.9 g. 1,4:3,6-dianhydrosorbitol (II), b_p 161°, m. 55-6°, [α]_D 45.36° (H₂O), and 2.1 g. of the 2- or 3-chloro-3c-in. of II, b_p 176-8°, m. 81°, heating sorbitol with 10 parts concd. HCl (20 hrs. at unstated temp. gave 30% sorbitol dianhydride, b_p 104-6°, m. 60-1°, and 21% (apparently) 3-chloro-3-deoxy-1,4:3,6-dianhydro-d-sorbitol, b_p 176-8°, m. 81-2°, [α]_D 37.9° (H₂O). Benzoylation of the latter in pyridine gave the dibenzoate, m. 101-2°, [α]_D 25.4° (CHCl₃), identified as that of 1,4:3,6-dianhydrosorbitol (cf. Wiggins, *Advances in Carbohydrate Chemistry* 5, 191, 220, 225 (1950)). If the syrup, obtained on heating sorbitol with concd. HCl as above, is treated in abs. EtOH with powd. KOH, satd. with CO₂, dried with Na₂SO₄, and evapd. the dianhydro deriv., b_p 162-5°, m. 60-1°, is formed. G. M. K.

DANILOV, S. N.

USSR/Chemistry - Polymerization

Card 1/1 : Pub. 151 - 11/37

Authors : Danilov, S. N., and Tikhomirova-Sidorova, N. S.

Title : The role of the oxidation-reduction characteristics of alpha-oxyketones during initiated polymerization

Periodical : Zhur. ob. khim. 24/3, 455-458, Mar 1954

Abstract : Experimental results indicate that the participation of hydroxycarboxylic compounds in oxidation-reduction systems during the polymerization of unsaturated compounds may serve as a means for the evaluation of their oxidation-reduction characteristics. The three keto-alcohol groups found most active in oxidation-reduction systems during polymerization are listed. Keto-alcohols, having played an important role as reducing agent in oxidation-reduction systems during polymerization, become oxidized; the cause for the oxidation is explained. Twelve references: 9-USSR; 1-USA and 2-German (1913-1954). Graph.

Institution : Academy of Sciences USSR, Institute of High Molecular Compounds

Submitted : December 1, 1953

DANILOV, S. N.

USSR/Chemistry - Isomerization

Card 1/1 : Pub. 151 - 12/37

Authors : Danilov, S. N., and Tikhomirova-Sidorova, N. S.

Title : Isomerization of alpha-oxaldehydes. Part 13.- Conversions of alpha-halo-
geno- and alpha-oxketones with primary alcohol group

Periodical : Zhur. ob. khim. 24/3, 458-465, Mar 1954

Abstract : Isomeric conversions of alpha-oxaldehydes were investigated to determine the role of primary alpha-keto-alcohols in oxidation-reduction conversions. It was found that primary keto-alcohols (propionylcarbinol and phenylacetol) do not isomerize in conditions of alpha-oxaldehyde conversion. It is assumed that the isomerization of alpha-oxaldehydes into secondary keto-alcohols does not proceed through the stage of primary keto-alcohol. The lesser reducibility of primary keto-alcohol, as compared with that of secondary alcohol, was confirmed by a polarographic method. Twenty-two references: 15-USSR; 1-Canadian; 2-French; 1-USA and 3-German (1890-1952). Table.

Institution : Academy of Sciences USSR, Institute of High Molecular Compounds

Submitted : October 29, 1953

DANILOV, S. N.

USSR/Chemistry - Polysaccharides

Card 1/1 Pub. 151 - 11/37

Authors : DaniloV, S. N., and Plisko, E. A.

Title : Study of chitin. Part 1.- Effect of acids and alkalis on chitin

Periodical : Zhur. ob. khim. 24/10, 1761-1769, Oct 1954

Abstract : The effect of alkalis (sodium or potassium hydroxide) at increased temperatures (up to 180°), and the effect of phosphoric acid on chitin were investigated. During repeated freezing and consequent defrosting of chitin partial hydrolysis of the acetyl group takes place at -40° and maximum hydrolysis was observed during the swelling and solution of the chitin. Complete solution of chitin was observed only at high phosphoric acid concentrations. The effect of high H_3PO_4 concentration on the solubility of chitin, is explained. Nineteen references: 12-German; 4-USSR; 2-USA and 1-Swiss (1880-1951). Tables; graphs.

Institution : Academy of Sciences USSR, Institute of High-Molecular Compounds

Submitted : February 23, 1954

Danilov, S. N.

Chitin. II. Glycerol ethers of chitin. S. N. Danilov and B. A. Plako. *Zhur. Obshchest. Khim.* 19, 2071-5 (1964); cf. C.A. 49, 8380f. — Dry chitin (5 g.) frozen and thawed 5 times in the presence of 90 ml. 30% NaOH, and the swollen and squeezed product triturated with 10 g. $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ in Me_2CO 48 hrs. at 60°, washed with H_2O , and neutralized with AcOH yielded 5.8 g. product which did not swell in H_2O or 4% NaOH. Repeated alkylation as above yielded the final product, analysis corresponded to $\text{C}_{11}\text{H}_{17}\text{O}_{10}\text{N}_2$, contg. 49% glyceryl residues; products with lower substitution are sol. in aq. H_2SO_4 and HCl , as well as H_3PO_4 , while the above product was insol. and was not swelled by NaOH. Chitin treated with NaOH as above, then with glycidol 12–30 hrs. at 50°, yielded products with up to 44.45% glyceryl residues; after 3-to-1 treatment, the product was $\text{C}_{11}\text{H}_{17}\text{O}_{10}\text{N}_2$. The products of low degree of substitution swell in AcOH and are sol. in mineral acids, while higher degree of alkylation resulted in products which swelled in 2–8% NaOH and even H_2O . The success of the reaction depends on the thawing technique. G. M. ...

DANILOV, S.N.

USSR.

Chemistry of cuprammonium solutions of cellulose. VI. Alcoholate copper atoms in cuprammonium complexes of cellulose. S. N. Danilov and M. G. Okun (Lensoviet Technol. Inst., Leningrad). *Zhur. Obshch. Khim.* 34, 2153-54 (1964); cf. *C.A.* 32, 1828⁴; 33, 4198⁴. Expts. on electrophoresis (with and without sepn. of the electrodes) of ammoniacal solns. of Cu and cellulose, alginate acid, sugars, and polyat. alcs. show conclusively that Cu separates only on the cathode (cf. Hess, *et al.*, *C.A.* 20, 664; 24, 1971). The Cu-cellulose complexes do not migrate to the anode, in either the presence or absence of NaOH. The hypothesis of a Cu alcoholate in cuprammonium cellulose is not confirmed, even by ion-exchange expts. When the solns. are passed through a cation exchanger NH₄ and Cu are absorbed, and the cellulose is pptd. on the resin. The passage of the solns. through an anion resin does not alter their compn. although the presence of Cu in the anion would have called for an adsorption of Cu on the anion resin. The cellulose-cuprammonium solns. can be regarded as mol. compds. of variable compn., caused by equil. reactions within them and can be compared to alkali cellulose. O. M. Kosolapoff

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DANILOV, S.A.

Hydrolysis of alginic acid and derivatives of d-mannuronic acid. S. N. Danilov and L. I. Rastorgova (Inst. High Pressure, Acad. Sci. U.S.S.R., Moscow). Zhur. Obshch. Khim. 25, 1590-1601 (1953); (Engl. transl. in Chem. Abstr. 48, 1590-1601 (1953)). Thesis, Leningrad, 1954. In the prepn. of alginic acid it is desirable to treat the macerated Na alginate with aq. HCl (0.5%) for sepa. from ash elements; after this treatment the product is extd. with MeOH. For hydrolysis of alginic acid it is best to use refluxing 90% HCO₂H in several stages, which yield completely pure d-mannuronic lactones. (1). The latter is difficult to isolate from hydrolyzates using alc. HCl. Ba mannuronate, (C₆H₇O₆)₂Ba, decomp. about 180°. [α]_D²⁰ 3.51°, with PhNHNH₂ forms phenylhydrazones, decomp. above 200°. Pure l. m. 143-4°, [α]_D²⁰ 92.84°. I treated with MeOH soln. of NH₃ gave l-aminomannuramide, decomp. 145°, [α]_D²⁰ -49.88° (after 10 min.) and shows mutarotation in aq. soln. I in alc. PhNHNH₂ yields the phenylhydrazone of d-mannuronic acid phenylhydrazones, decomp. 166°, [α]_D²⁰ 14.68° (pyridine). I with Ac₂O-ZnCl₂ gave triacetyl-l. m. 119-20°, [α]_D²⁰ 139.84° (dry CHCl₃). I with alc. EtSH gave l diethylmercaptal, a sirup, which forms a triacetate, m. 103-4°, [α]_D²⁰ 36.72° (MeOH). I in concd. HCl treated with PhCH₂SH gave 80% l dibenzylmercaptal, m. 44-6°, [α]_D²⁰ 125° (MeOH). The soln. of I in N HCl in MeOH treated with excess PhCH₂SH and kept 1.5 hrs. yields, apparently, the Me ester of mannuronic acid benzylmercaptal, a sirup; this with Ac₂O gave Me 1,3,4,5-tetraacetylbenzylmercaptal, d-mannuronate, m. 95-6° (crude), m. 96-7° (from MeOH), [α]_D²⁰ 164.94° (in CHCl₃). I dibenzylmercaptal treated with Ac₂O in pyridine gave 67% product, C₂₄H₂₈O₈S₂, m. 147-9°, [α]_D²⁰ 99.93°, whose acetate does not form a phenylhydrazone nor does it form Me esters on heating in MeOH. G. M. Kosolapoff

DANILOV, S. N.

✓ Anhydrides and amino and guanidino derivatives of carbohydrates and polyatomic alcohols. III. Amination and guanidination of carbohydrates: S. N. Danilov and I. S. Lishanskii (Inst. High Mol. Wt. Comp., Moscow). *Zhur. Obshch. Khim.* 25, 2106-17 (1953); cf. C.A. 49, 6840c. Refluxing 30 hrs. 4.1 g. 1,2,3,6-diisopropylidene-3,6:4,5-lactone with 100 ml. alc. guanidine contg. 1.18 g. guanidine gave a ppt. of guanidine *p*-toluenesulfonate and 70% 1,2,3,6-diisopropylidene- α -D-glucopyranose. m. 110-111°; similar lack of guanidination was found in anal. expts. at 140°. A similar result was obtained with 1,2,3,4-diisopropylidene-6-O-tosylgalactose. Treatment of cellulose with 18% NaOH, followed by MeSO₂Cl gave a product with 1.3-1.7 sulfonate groups per glucose unit, which did not even swell in org. solvents. Treatment of this material with liquid NH₃ up to 140° gave products with up to 4.2% N and 12-14% S. Cellulose partially oxidized with HIO₄ and reacted with NH₃ rather readily, yielding products susceptible to wool dyes. Keeping 45 g. α -Me 4,6-benzylidene-glucoside with 115 g. *p*-MeC₆H₄SO₂Cl in 200 ml. dry pyridine 10 days gave upon treatment with ice and dil. HCl 94-8% α -Me 2,3-di-O-*p*-MeC₆H₄SO₂-4,6-benzylidene-glucoside, m. 148-9°. This (22.2 g.) in dry (CH₂Cl)₂ was treated rapidly with 5.2 g. Na (14 hrs.); after diln. with (CH₂Cl)₂ and washing with H₂O there was obtained 94% α -Me 1,3-anhydro-4,6-benzylidene-allanide (I), m. 199-200° (the use of theoretical amount of MeONa gives much unreacted material). This heated with MeOH-NH₃, 72 hrs. at 100° gave 91% α -Me 2-deoxy-2-amino-4,6-benzylideneallanide (II), m. 163-9°; HCl salt, m. 129-30°; picrate, m. 181-2°. An apparent 2-amino isomer of this substance, m. 141-3°, was obtained from the mother liquor in sepn. of the 2-amino deriv. above. II with Ac₂O-pyridine in 3 days gave the 2-acetamide analog, m. 181-2° (cf. Wiggins, C.A. 41, 3424c). II with HN:C(SMe)₂ caused only the decompn. of the latter. Treatment of

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It with $\text{HN}(\text{C}(\text{OMe})\text{NH})_2$ gave only a trace of guanidine
 deriv.; picrate, m. 118-22°. Heated with MeOH-MeNH_2
 in autoclave 75 hrs. at 100° gave 80% α -Me-2-deoxy-2-
 methylamino-1,6-benzylideneallitroside, m. 125-6°; HCl salt,
 m. 135-6°; picrate, m. 165-6°. Heating I with guanidine in
 pyridine contg. a little H_2O 10 hrs. at 100° gave a 25% yield
 of α -Me-2-deoxy-2-guanidino-1,6-benzylideneallitroside, m.
 145-7°; no reaction took place in Me_2CO , while in MeOH
 soln. the latter added to I, yielding 2-Me-2-methyl-1,6-benz-
 ylidenallitroside. I heated with monoacetylguanidine also
 gave the same product. I and guanidine-HCl in dry MeOH
 after 60 hrs. at 140° gave α -Me-3-chloro-1,6-benzyl-
 ideneallitroside, m. 162°.

G. M. Koschupoff

DANILOV, S.M.

In memory of M.M. Zinin, founder of the Russian school of organic chemists; on the 75th anniversary of his death. Zhur.ob.khim. 25 no.13:2353-2374 D '55. (MLBA 9:3)
(Zinin, Nikolai Nikolaevich, 1812-1880) (Chemistry, Organic)

DANILOV, S. N.

"Molecular Regrouping and Intramolecular Oxidation-Decoxidation" a chapter from the book Reactions and Methods of Investigation of Organic Compounds, Vol. 4, publ. by State Sci. Tech. Publ. House for Chem. Lit., Moscow, 1957.

DANILOV, S.N.

Work practice of the Leningrad Branch of the Society. Khim.nauka
i prom. 1 no.5:599-600 '56. (MLRA 9:12)

1. Chlen-korrespondent Akademii nauk SSSR.
(Chemical societies)

DANILOV, S.N.

Chemistry of cuprammonium solutions of cellulose. VII.
Reaction of polyhydroxy compounds with the amine complex of copper. S. N. Danilov and M. G. Okun (Leningrad Technol. Inst., Leningrad). *Zhur. Obshchei Khim.* 26, 3005-14 (1958); cf. C.A. 49, 9283g. The compn. of ppts. formed on addn. of NaOH or LiCl to cuprammonium cellulose solns. (I) was examd. and the spectra of I were detd. The ppts. have variable compn., and the molar ratio of cellulose to Cu can be regarded as approximating 1:1, but not necessarily equaling this value; with excess NaOH the Cu is replaced totally to give an alkali cellulose of the approx. compn. $2C_6H_{10}O_5 \cdot NaOH$. No stoichiometric regularities, as reported by Normann [*Chem. Ztg.* 30, 684 (1908)], could be confirmed in the ppts. The spectra of I and of Fehling soln. (these are reproduced) are quite unlike those of Cu acetate or sulfate; this indicates a definite chem. interaction in the I. I, methylcellulose, hydroxyethylcellulose, oxycellulose, sucrose, glucose, glycerol, alginic acid, Na alginate, tartaric acid, and Cellophane were examd. spectrographically from 2000 Å. to 1 μ. $Cu(OAc)_2$ has an abs. min. at 480-510 mμ and absorbs continuously from 600 mμ; $CuSO_4$ shows a band at 400-575 mμ, has a max. at 800 mμ beyond which the optical d. gradually decreases; cuprammonium reagent has a band of 235-250 mμ, with addnl. min. at 420 mμ and a max. at 640 mμ; Fehling soln. absorbs totally at 380 mμ, has a min. at 440 mμ, and a max. at 670 mμ. Cuprammonium solns. of the lower saccharides are essentially duplicates spectroscopically of the cuprammonium soln., with slightly increased optical d. at 320-460 mμ; tartaric acid has a min. at 433 mμ and a max. at 640 mμ. Cuprammonium cellulose has a max. at 640 mμ and a min. at 420 mμ, the same being true of the cellulose derivatives. These results indicate the absence of specific compds. between the cellulose and the amine complexes. The soln. in Schweizer reagent is a colloid-chem. phenomenon with possible formation of unstable intermol. compds. G. M. Kosolapoff

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DANILOV, S.M.; GINTSE, N.F.

Role of phosphoric acid in the study and processing of cellulose.
Part 1. Swelling and dissolution of cellulose in phosphoric acid.
Zhur.ob.khim.26 no.11:3014-3020 N '56. (MIRA 10:1)

1. Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR.
(Cellulose) (Phosphoric acid)

LAMILEV, S. P., and KUNZ, M. A.

"Investigation of Polymerization," a paper presented at the 1st Congress
on the Chemistry and Physics of High Polymers, 2nd Session, 1964, Prague,
Czechoslovakia.

See, also, 1964

"Don't let it go," said the man who had been talking to me.
"It's a good thing you're here," he said, "because I'm
going to tell you something that will make you think about
it all over again."

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DANIKOV, S. N.

Distr: 4E4j/4E3d/4E2c(j)

⁷
Anhydrides and amino and guanidino derivs. of carbo-
hydrates and polyatomic alcohols. ⁷V. Derivatives of mono-
and dianhydrides of xylitol. S. N. Danilov, A. N. An-
kova, N. S. Tikhomirova-Sidorova, and A. N. Shirokova
(High Polymer Inst., Acad. Sci. U.S.S.R., Leningrad).
Chem. Abstr. 21, 2104-10 (1957); cf. C.A. 49,
6840; 52, 2600a. — Keeping xylitol with Pb_2Cl_2 in pyri-
dine 2 days gave after aq. treatment 3-trityl-1,4-anhydroxy-
litol, m. 80°; diacetate, m. 134-5°. This gave 3,4-diacetyl-
5-tritylxylitol, $C_{24}H_{28}O_{10}$, m. 146-7°. Xylitol and p-
 $MeC_6H_4SO_2Cl$ in pyridine gave 25% 2,3,5-tritosyl-1,4-
anhydroxylitol, m. 106°. Treatment of xylitol with $SOCl_2$
with ice cooling gave in 5 days 3,5-thionyl-1,4-anhydroxylitol,
m. 83-4°; this with $Ac_2O-NaOAc$ gave 2-acetyl-3,5-thionyl-
1,4-anhydroxylitol, b.p. 105-7° d₄ 1.4281, n_D 1.4510;
use of H_2Cl in pyridine gave in 2 days 2-benzoyl-3,5-thionyl-
1,4-anhydroxylitol, m. 90-8°. The thionyl deriv. with
tosyl chloride in pyridine gave in 12 hrs. 3-tosyl-3,5-thionyl-
1,4-anhydroxylitol, m. 80-1°. Heating xylitol with para-
formaldehyde in presence of concd. HCl 8 hrs. at 60° and
allowing the mixt. to stand overnight gave 3,5-methylene-
1,4-anhydroxylitol, m. 77°, b.p. 138-9°; benzoate, m. 113°;
tosylate, m. 88°. Xylitol and BzH in concd. HCl gave
benzylidenexylitol, m. 139°, best prepd. from xylitol and
 BzH by heating in CO_2 stream at 160° 3 hrs.; benzoate,
m. 133°; tosyl ester, m. 110°. Refluxing 134 g. xylitol with
3 parts Me_2CO in presence of 80 g. $CuSO_4$ 20 hrs. gave 81%
isopropylidene deriv. of xylitol, m. 65° ($Et_2O-EtOH$);
benzoate, m. 79.5-80°; tosyl ester, m. 84°. Xylitol and
cyclohexanone shaken in Et_2O with a little H_2SO_4 10 hrs.
gave cyclohexylidenexylitol, b.p. 155-6°, n_D 1.5034; benzo-

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S. N. DIMITROV, A. A. ANTONOVA

ate, m. 104-8°; tosyl ester, 2-tosyl-3,5-cyclohexyldiene-1,4-anhydrosorbitol, m. 96°. Isopropylidenexylitol and PhNCO in CHCl₃ after 6 hrs. at 100° gave 3,5-isopropylidene-1,4-xylitol urethan, m. 107-8°. Similarly was prepd. 3,5-benzylidene-1,4-xylitol urethan, m. 187-8°. Heating isopropylidene- or cyclohexylidenexylitol benzoates with 80% AcOH 45 min. gave the same monobenzoate, m. 91-2°, with the benzoate group on position 2 as shown by oxidation with Pb(OAc)₂. Treatment of well-dried xylitol or xylitol with dry HCl at 105° gave after neutralization with Na₂CO₃ a syrup which crystd. in 1-2 days to xylitol chloride, m. 48-9°, b_p 160-1°, d₄ 1.40-1°, d₂₀ 1.3722, n_D 1.5030. This with tosyl chloride in pyridine gave 51% 1,3-ditosyl-5-chloro-1,4-anhydrosorbitol, m. 102°. The chloride and PhNCO at 100° gave xylitol chloride phenylurethan, C₁₂H₁₅O₅NCl, m. 137-8°, while with excess PhNCO at 150° there formed the bis-(phenylurethan), m. 181-2°, 1-chloro-3,4-dicarbonylo-1,4-anhydrosorbitol. Treatment of xylitol chloride with MeONa in the cold gave 78% 1,4,3,5-dianhydrosorbitol, b_p 120-1°, d₄ 1.18-16°, b_p 62°, d₂₀ 1.3506, n_D 1.4902; acetate, b_p 92°, n_D 1.4572; benzoate, m. 84°; tosyl ester, m. 90-5°; phenyl urethan, m. 114°. G. M. Kozlov

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AUTHORS: Danilov, S. N., Gintse, M.F.

79-12-24/43

TITLE: The Chemistry of Xanthogenates and Viscose (Kimiya ksantogenatov i viskozy).
VI. The Interdependence of Viscose Components (VI. Vzaimootnosheniya komponentov viskozy).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 12, pp. 3296-3301 (USSR).

ABSTRACT: In the present experiments the effect of the concentration of sodalye as well as of some salt components of viscose (NaS , Na_2CS_3 , Na_2CO_3 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$) in aqueous and alkaline solutions on the velocity of decomposition of cellulose xanthogenate are investigated. In order to determine the transformation of viscose xanthogenate and the sulfur products forming on this reaction various chemical methods and also potentiometric titration were used. In aqueous solutions xanthogenate decomposes quicker than in alkaline solutions, where with the increase of the alkaline character of the solutions of xanthogenate also the steadiness with regard to the formation of gelatine increases. The decomposition of xanthogenate in weak salt solutions takes place with a velocity which is close to that in water. The more concentrated the salt solution is, the less intensive is the decomposition.

Card 1/2

The Chemistry of Xanthogenates and Viscose.

79-12-24/43

VI. The Interdependence of Viscose Components.

The addition of sodiumhydroxide to the salt solution stops it as is the case in pure alkaline solutions. The nature of the salt additions plays a certain part in the formation of gelatine of aqueous salt solutions. A strange influence on the decomposition of xanthogenate exercises sodiumsulfite by slowing down its own aging in dependence on the decomposition products being formed. With the decomposition of cellulose xanthogenate in aqueous and aqueous electrolytic solutions, as well as of ordinary viscose considerable quantities of sodium sulfite are formed primarily, which then reacts with carbon disulfide and forms trithiocarbonate. The latter can, however, produce again sodium sulfite by means of hydrolysis. The content of sodium sulfite decreases with the storing (maturing-yozrevaniye) of the solutions of purified xanthogenate whereas the content of trithiocarbonate increases.

There are 10 figures, 1 table, and 17 references, 6 of which are Slavic.

ASSOCIATION: Institute for High-Molecular Compounds AN USSR (Institut vysokomolekulyarnykh soyedineniy Akademii nauk - SSSR).

SUBMITTED: February 8, 1956.

Card 1/2 : 1. Xanthogenates-Deterioration 2. Cellulose-Deterioration
3. Xanthogenates-Titration 4. Cellulose-Titration

DANILOV, S. N.

Distr. 1/E13 7
Isomerization of α -hydroxy aldehydes. XIV. Synthesis
 of derivatives of glyceraldehyde/ S. N. Dantlov and V. I. Ivanchenko (Leningrad, *Izv. Akad. Nauk SSSR, Khim. i Tekhn. Org. Sint.*, 1983, 22, 2093-6(1987); cf. C.A. 49, 8113f.
 Heating acrolein and an equimolar amt. of Ac₂O in sealed vessel with 8% CuCl₂ inhibitor 7 hrs. at 100° gave acrolein diacetals, b_p 72-4°, d₄ 1.0720, n_D 1.4215. This (50 g.), 81 moles AcOH, and 40-50 g. NaOAc chlorinated over 8-7 hrs. at 0-9° and either extd. with Et₂O and washed with H₂O, or concd., extd. with Et₂O, and distd. yielded 40% **AcOCH₂CH(Cl)CH(OAc)**, b_p 123-4°, d₄ 1.2552, n_D 1.4420; phenyllosazone, m. 82°; **3,6-dinitrophenyllosazone**, m. 278°. Treatment of acrolein with 6-8 parts MeOH and 1% hydroquinone and excess chalk with a stream of Cl at room temp. gave a mixt. of products from which were isolated: **1-chloro-3-methoxylglyceraldehyde**, dichloroacrolein, and their Me acetals; heating the mixt. with 6% H₂SO₄, 3-5 hrs. at 60° followed by neutralization and distn. in CO₂ atm. gave 25% **1-chloro-3-methoxylglyceraldehyde**, b_p 83.6-4°, d₄ 1.1851, n_D 1.4420, which failed to form a phenyllosazone, but gave **3,6-dinitrophenyllosazone of 3-methoxylglyceraldehyde**, m. 282°. G. M. Kosolapoff

G. M. Kosolapoff

DANILOV S N

BUTLEROV, Aleksandr Mikhaylovich; TEREHT'YEV, A.P., otvetstvennyy red.;
DANILOV, S.N., red.; PLATE, A.P., red.; POROSHIN, K.T., red.;
BYKOV, G.V., red.izd-va; PAVLOVSKIY, A.S., tekhn.red.; MAKUN, Ye.V.,
tekhn.red.

[Works] Sochineniia. Moskva, Izd-vo Akad. nauk SSSR. Vol.3.
[Popular scientific, historical, critical, bibliographical and
other works in chemistry. Travels] Nauchno-populiarnye, istoriche-
skie, kritiko-bibliograficheskie i drugie raboty po khimii.
Puteshestviia. 1958. 429 p. (MIRA 11:4)

1. Chlen-korrespondent AN SSSR (for Terent'yev, Danilo)
(Chemistry)

10/10/58

AUTHOR: Sergiyenko, I. Z.

REV/ 30-5'-6-30/45

TITLE: The Chemistry and Metabolism of Carbohydrates in Animal and Plant Organisms (Khimiya i obmen uglevodov v zhivotnom i rastitel'nom organizmakh) Conference in Moscow (Konferentsiya v Moskve)

PERIODICAL: Vestnik Akademii nauk SSSR, 1958, Nr 6, pp. 112-114 (USSR)

ABSTRACT: This conference took place from January 28 to January 30. It was organized by the Laboratory for Physiological Chemistry of the AS USSR and was attended by about 200 specialists, among them organochemists, biochemists, physiologists, pharmacologists, histologists and physicians who represented various scientific institutions of the AS USSR, of the Academy of Medical Sciences of the USSR, of the VASKhNIL, of a number of universities and other colleges, as well as of branch institutes from all the country. It was opened by the Director of the Laboratory for Physiological Chemistry B. N. Stepanenko. He stressed in his detailed report among other things the great theoretical interest in the investigation of the ab-

Card 1/5

301, 30-53-6-30/45

The Chemistry and Metabolism of Carbohydrates in Animal and Plant Organisms.
Conference in Moscow

solute formation of simple carbohydrates. New and great success was achieved in the field of the O- and N-glycosides. He reported on some important results of the work in laboratories. Furthermore the following reports were heard:

- 1) S. N. Danilov: On the reaction of the simultaneous oxidation and regeneration in a group of carbohydrates.
- 2) Yu. A. Zhdanov: On the use of different methods of synthesis.
- 3) B. N. Stepanenko, L. K. Kryukova, O. G. Seriyuk: On investigations carried out in the field of some O- and N-glycosides.
- 4) O. K. Orlova: On 2 new diphtheria bacilli.
- 5) Ye. K. Alimova: On carbohydrates in the structure of diphtheria bacilli.
- 6) S. A. Neyfakh and M. P. Mel'nikova: On enzymatic members.
- 7) V. S. Il'in: On the importance of hexokinase reaction.

Card 2/3

AUTHORS: Danilov, S. M., Plisko, Ye. A. SOV/79-28-8-45/66

TITLE: Investigation of Chitin (Izucheniye khitina) III. Hydroxy-Ethyl- and Ethyl Ether of Chitin (Oksietilovyye i etilovyye efiry khitina)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2217 - 2223 (USSR)

ABSTRACT: The authors had previously pointed out that the synthesis of chitin ether is made difficult by the fact that chitin is swelling very little in the solutions of alkali (Ref 1). The investigation of the heats of swelling (Ref 2) in solutions of sodium hydroxide shows that the reaction of chitin is inhibited by the lye. In former attempts to attain the hydroxy-ethyl ethers of chitin it was found that these are not formed under the same conditions as in the synthesis of the hydroxy-ethyl ethers of cellulose. The etherification- and activation conditions with alkali liquor were varied: chitin was treated with alkali during freezing, the etherification was carried out at higher temperature which took more time. Besides, the chitin was used in the etherification in various states of pulverization whereat the molecular

Card 1/3

Investigation of Chitin. III. Hydroxy-Ethyl- and
Ethyl Ether of Chitin

SCV/73-26-6-45/66

ratio between it and the ethyleneoxide was also varied. Hydroxy-ethyl ethers of a high degree etherification were obtained which are soluble in water and diluted sodium hydroxide. The ethylation of the chitin treated with alkali liquor was performed with ethyl chloride in sealed tubes in the autoclave. The newly synthesized ethyl-ethers of chitin are soluble in alcohols, ketones, hydrocarbons and esters. The films from ethyl chitin are equal to those from ethyl cellulose as far as their durability is concerned. There are 3 figures, 4 tables, and 7 references, 5 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR
(Institute of High-Molecular Compounds, AS USSR)

SUBMITTED: July 4, 1957

Card 2/3

AUTHORS: Danilov, S.N., Gintse, N.F., Levitskaya, A.V. SOV, 73-28-11-10, 65

TITLE: Chemistry of Xanthates and Viscose (Khimiya ksantogenatov i viskozy)
VIII. Investigation of the Polysulfur Compounds and of the Composition of Viscose Using Tracer Atoms (VIII. Izucheniye polissernistykh soyedineniy i sostava viskozy s primeneniye tekhenykh atomov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 11, pp 2948-2958 (USSR)

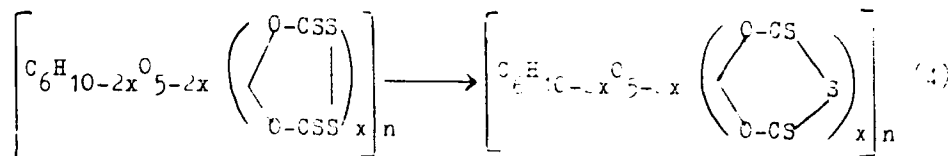
ABSTRACT: In the present experiments the separation of the sulfur atom from dioxanthogenides of cellulose, and of ethyl alcohol from sodium disulfide and sodium perthiocarbonate containing the radioactive sulfur isotope S^{35} in their molecules is dealt with. The results of these experiments are compared to those of the usual chemical analysis. This radioactive method makes it possible to determine the composition of viscose, i.e. the amount of polysulfur compounds, the distribution of carbon disulfide for the formation of its components. This determination was carried out much more rapidly than by the usual analytical methods. The danger of the mutual exchange of radioactive and normal sulfur atoms within the molecule and between the molecules is best removed by sodium cyanide as sulfur acceptor. The dioxanthogenides form thioacid anhydrides on the

Card 1/3
2

Chemistry of Xanthates and Viscose. VIII. Investigation of the polysulfur Compounds and of the Composition of Viscose Using Tracer Atoms

SOV 77-28-11-10 55

separation of one sulfur atom:



Compared with the calculated values the dixanthogenide of cellulose in these experiments separates more sulfur which is probably due to the unstable behaviour of the thioacid anhydrides in alkaline media. Thus, the separation of sulfur from the dixanthogenides of cellulose and of ethyl alcohol from sodium disulfide and sodium perthiocarbonate was investigated by means of radioactive atoms and according to the usual analytical method. The radioactive method of separation makes it possible to carry out rather exactly the separation of sulfur from sodium disulfide and sodium perthiocarbonate by means of sodium sulfite and sodium cyanide.- There are 9 tables and 13 references, 7 of which are Soviet.

Card 2/2

Inst Higher Molecular Compounds AS USSR

AUTHORS: Danilov, S. N., Lopatenko, A. A. SOV. 79-25-12-4/41

TITLE: Anhydro, Desoxy, and Unsaturated Derivatives of Polysaccharides (Angidro-, dezoksi- i nenasyshchennyye polivodnyye polisakharidy) I. Desoxy Cellulose From Cyanoethoxyl Cellulose (I. Dezoksitsellyuloza iz tsianoetoksitsellyulozy)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3184-3188 (USSR)

ABSTRACT: Deoxidized monoderivatives with methylene groups in the place of secondary alcohol groups (desoses), and with methyl groups in the place of primary alcohols (methyloses) may be found in Nature and can be synthesized in different ways. Until now only few syntheses of deoxidized celluloses of the formula $(C_6H_7O_{5-x})_n$ have been published, predominantly with methyl groups obtained by way of tosyl ethers and iodine derivatives. To obtain these celluloses also their iodine derivatives and their unsaturated compounds were reduced (Refs 1,2) The general synthesis of the deoxidized celluloses with methylene and methyl groups were realized by P. P. Shorygin by the cleavage of ether with sodium, especially

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in liquid ammonia (Refs 3,4). Shorygin and his cooperators used the cleavage reaction of the ethers with Na in liquid ammonia also with methylated sugars, methyl cellulose, benzyl ethers of cellulose and acetyl cellulose (Refs 5-9). Positive results were obtained in the deoxidation of cellulose only in the case of methyl cellulose, however, only a partially deoxygenized methyl cellulose resulted. First the authors processed the industrially produced ethyl cellulose (Ref 10) (46.8%OC₂H₅) with Na in liquid ammonia, yet no sufficient separation of the ethoxyl groups occurred. Based on theoretical considerations an easier separation of the cyanoethoxyl groups could be expected when using cyan ethoxyl cellulose. Cellulose actually completely loses these groups, partly as acrylic acid, with methylene and partly methyl groups forming in the place of alcohol groups in the glucose members. Desoxy cellulose is formed as the final product. Part of the cyanoethoxyl groups separates under the formation of desoxy groups, another part as acrylonitrile, due to the reversible cyanoethylation reac-

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Anhydro, Desoxy, and Unsaturated Derivatives of
Polysaccharides. I Desoxy Cellulose From
Cyanoethoxyl Cellulose

DOI, 79-28-12-4/41

tion in the alkaline medium. The presence of desoxy groups
in the reaction product is proved by the analysis of the
final product, its acetate and nitrate. There are 1 table
and 13 references, 8 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Leningveta
(Leningrad Technological Institute imeni Leningvet)

SUBMITTED: January 6, 1958

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AUTHORS: Denisov, S. N., Lopatenko, A. A. SOV. 74-28-12-5/41

TITLE: Anhydro, Desoxy, and Unsaturated Derivatives of Polysaccharides (Angidroz, dezoksi- i nenasyshchennyye proizvodnyye polisakharidov) II. Synthesis of Anhydrocellulose From Esters of p-Toluenesulfonic Acid III. Sintez angidrotsellyulozy iz p-toluolsul'fokislotsnykh efirov

PERIODICAL: Zhurnal obshchey khimii 1958, Vol 28, No 12, pp 3189-3191 (USSR)

ABSTRACT: Besides other syntheses of anhydrocellulose (Ref 1) only one paper exists (Ref 2), in which its synthesis is described in the form of its mixed tosyl- and acetic ester from the mixed acetic and tosyl-ester of cellulose on the action of caustic soda in methyl alcohol. The composition of anhydrocellulose corresponds to the formula $[C_6H_7O_2-2xO_5-x]_n$. For its synthesis the tosyl esters of the cellulose $[C_6H_7O_2-2xO_5-x(OSO_2C_6H_4CH_3)_x]_n$ were treated with sodium in liquid ammonia or with organic bases (piperidine etc.) (Ref 3). The use of piperidine yielded final products which were difficult to characterize (Ref 4). Samples of anhydrocellulose are described in the experimental

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Anhydro, Desoxy, and Unsaturated Derivatives of
Polysaccharides. II. Synthesis of Anhydrocellulose
From Esters of p-Toluenesulfonic Acid

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part, which were obtained on the action of sodium in liquid ammonia on tosyl cellulose, the composition of which could be proved by its analysis and that of its acetic esters. As the tosyl groups in the cellulose enter mainly the primary, partly also the secondary, and only to a small extent the tertiary alcohol group, the authors could determine the position of the anhydride nucleus in the above anhydrocellulose samples with high probability. On the action of sodium on liquid ammonia the p-toluenesulfonic acid separates under the formation of the anhydro nuclei from the tosyl esters of cellulose which contain more than 1 tosyl group per 1 glucose member; the other tosyl groups are subjected to hydrolysis. There are 2 figures and 5 references, 1 of which is Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Lensovet
(Leningrad Technological Institute imeni Lensovet)

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acceptor → -S - S - acceptor

SOV, 79-23-12-6/41

Chemistry of Xanthates and Viscose. IX. The Detection of Polysulfur Compounds in Viscose and the Part Played by Them

The chemical transformations which are important in the course of ripening of viscose take place with the xanthate of cellulose, sodium sulfite, sodium thiocarbonate etc. Whereas the entire content of polysulfur compounds in viscose is determined by means of sodium cyanide and sodium sulfite, the separate determination of their content by means of the potentiometric method is very difficult, especially in the presence of alkali. The xanthate can be liberated from side compounds by activated carbon and anionites. The course of the curve of optical density of the viscose solutions and alcoholic solutions of trithiocarbonate are the same; in the aqueous solutions of trithiocarbonate sodium disulfide was found by the hydrolysis and oxidation of the former. In the viscose solution there is a large quantity of trithiocarbonate and a small amount of perthiocarbonate. Figures 1, 2, 3 present the comparative potentiometric titrations of the salt solutions with silver nitrate considered in the investigation (solutions of sodium sulfite, sodium thiosulfate, trithiocarbonate, perthiocarbonate, sulfide, disulfide, etc.) The spectrographic investigations aimed at detecting the polysulfur compounds of sodium disulfide and perthiocarbonate to

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Chemistry of Xanthates and Viscose. I. The Detection of Polysulfur Compounds in Viscose and the Part Played by Them

find these compounds in viscose. In figure 4 the dependence of the optical density of the solutions on the wave length is given.- There are 4 figures and 20 references, 12 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR i Leningradskiy khimiko-tekhnologicheskiy institut imeni Lensovet (Institute of High-Molecular Compounds, Academy of Sciences USSR, and Leningrad Chemotechnological Institute imeni Lensovet).

SUBMITTED: January 23, 1958

Card 3/3

DANILOV, S.N.; SIDOROVA-TEKHOMIROVA, N.S.; KULAKOVA, O.M.

Emulsion xanthogenation. Zhur. prikl. khim. v. 31 no.5:765-771
My '58. (MIRA 11:6)
(Emulsions) (Xanthic acid)

DANILOV, S.N.

Importance of A.E.Favorskii's reaction and theoretical views in modern chemistry industry. Izv.vys.ucheb.zav.;khim.i khim.tekh. 3 no.4:761-771 '60. (MIRA 13:9)

(Chemistry, Organic)
(Favorskii, Aleksei Evgrarovich, 1860-1941)

SECRET
JG 13-4-6-13

AUTHOR: Danilov, S. M. (Corresponding Member of the USSR Academy of Sciences)

TITLE: Cellulose and Other Hexosans as Starting Materials in Organic Synthesis

PERIODICA: Khim. i tekhn. sel'sk. khoz. (USSR), 1974, No. 1, pp. 13-14 (USSR)

ABSTRACT: This is a review (based on literature data) of methods for converting cellulose and other hexosans into the starting materials in organic syntheses. The following methods and materials were discussed: hydrolysis, alcoholysis, mercaptolysis, solvolysis, and fermentation of polysaccharides (including the preparation of furfural from polyurides and oxycelluloses); hydrogenolysis of polysaccharides and hydrogenation of monoses; thermal cleavage of polysaccharides (formation of formaldehyde, ethylene glycol, furfural, and other); acid dehydration of polysaccharides and monoses with the formation of,

PHASE I BOOK EXPLOITATION

SCV/4523

Leningrad. Universitet

Voprosy teorii stroyeniya organicheskikh soyedineniy (Problems in the Theory of the Structure of Organic Compounds) [Leningrad] 1960. 239 p. Errata slip inserted. 3,725 copies printed.

Sponsoring Agency: Leningradskiy ordena Lenina Gosudarstvennyy universitet im. A.A. Zhdanova.

Resp. Ed.: T.A. Favorskaya; Ed.: V.D. Piastro; Tech. Ed.: S.D. Vodolagina.

PURPOSE: This collection of articles is intended for chemists and organic chemists.

COVERAGE: The collection is concerned with the scientific legacy of A.Ye. Favorskiy, and includes discussions of his theoretical views and their evolution in connection with the development of theoretical organic chemistry. The articles review problems on the structure, reactivity and transformations of various classes of organic compounds: unsaturated acyclic and cyclic hydrocarbons, saturated and unsaturated alcohols, glycols and carbonyl compounds. No personalities are mentioned. References accompany each article.

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Problems in the Theory of the Structure (Cont.)

SOV/4583

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DANILOV, S.N.

Mechanism of the intramolecular redox reaction in the group of α -hydroxy- and α -halocarbonyl compounds. Izv. AN SSSR. Otd. khim. nauk no. 12:2118-2126 D '60. (MIRA 13:12)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Oxidation-reduction reaction) (Carbonyl compounds)

DANILOV, S.N.

Course of the simultaneous oxidation-reduction reactions of organic compounds, and their biochemical and technical importance. Trudy LTI no.60:5-31 '60. (MIRA 14:6)

(Oxidation-reduction reaction)

1.7400

1.7400

AUTHORS: Dmillov, S. N., Andriyenko, A. M., Lashchenko, A. A.

TITLE: Isomerization of Hydroxyaldehydes. II. Acid Trans-
Formations of Glycosylaldehydes and Their Derivatives

PERIODICAL: Zhurnal Obshchei Khimii, 1977, Vol. 47, No. 7,
pp. 1777-1784 (USSR)

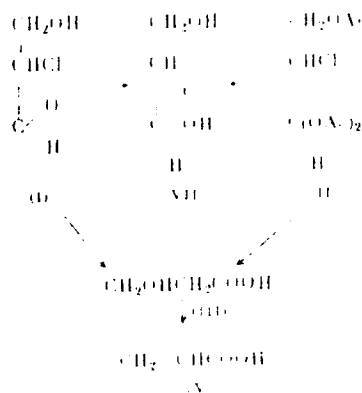
ABSTRACT: Optho-maccharinic acid was obtained by S. N. Dmillov
and A. M. Gakhovskiy (this Journal, 1977, Vol. 47, 706;
Ber., 1976, Vol. 49, p. 1136) in reaction of β -halo-
substituted monoses with acid hydroxide. It was expected,
therefore, that monoses containing unsubstituted
hydroxyls at C₂ and C₃, with glycosylaldehyde replaced
by substituents stable to acid hydroxide, will
isomerize similarly in reaction with $\text{Pr}(\text{OH})_3$ into
o-maccharinic acid. It was shown that (1+1) gly-
cosylaldehyde (V) isomerized to o-maccharinic acid with freshly
precipitated $\text{Pr}(\text{OH})_3$ to give o-maccharinic acid (VI) whereas

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Isomerization of Hydroxyaldehydes. *XI*

307/1 (1-5-17/6)

Its halo derivatives, α -chloro- β -hydroxyaldehyde (I) and 1,1,1-trichloro- α -chloro- β -hydroxyaldehyde (II) gave hydroxyaldehyde (III), which was transformed further into (IV).



(Eq. 1-1-17/6)

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Isomerization of Hydroxy aldehydes 27

307/1 - 100 - 100



The oxidation-reduction of I and II proceeds here with the participation of H atom in α position with respect to the aldehyde group, and the reaction can be explained by the formation of α -aldehydes (VII). The oxidation-reduction of the β -aldehyde (V) takes place between the aldehyde radical and the β -aldehyde radical; the transformation of V into β -aldehyde (VI) can be interpreted as proceeding through the β -aldehyde (VIII). Considering the above, the formation of β -aldehydes from monomers can be explained by the α - and β -aldehydes compounds. β -Aldehydes contribute chiefly to the oxidation-reduction transformation of

and 1/2

Isomerization of Hydroxyaldehydes. XV

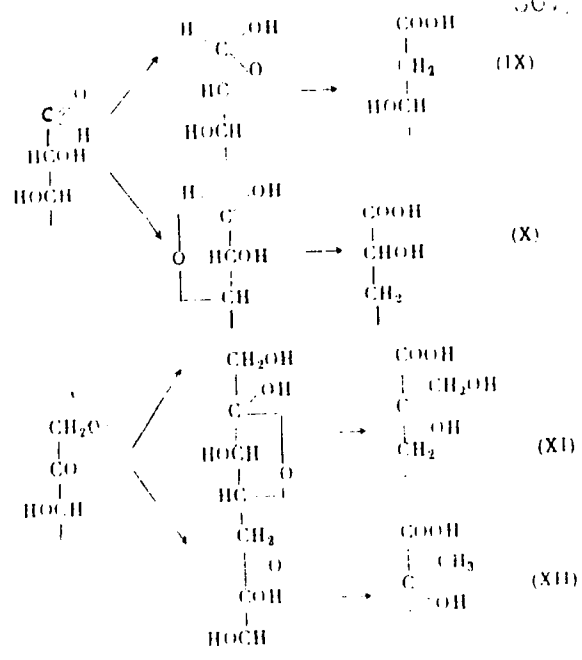
[Chem. Abstr. 307, 14-64-74, 1974]

aldehydes, whereas the formation of anomeric alcohols (IX) from halo monosaccharides can be best represented as occurring through α -glycosides. The following mechanism of anomeric alcohols formation are proposed: (i) isomerization of aldehydes into anomeric alcohols through β -glycoside compounds (X); (ii) the formation of anomeric alcohols is normally linked with the migration of β -glycoside ketones (XI) with migration of the H atom into β -position; (iii) the formation of anomeric alcohols from ketones goes through the α -glycoside (XII); (iv) the formation of anomeric alcohols (XIII) is suggested as occurring with the migration of the H atom into β -position.

<...> alcohols with migration of H atom into β -position to the fourth carbon atom.

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Isomerization of Hydroxyethylol XV



Cont. 1/6

Isomerization of Hydroxyaldehydes. XV

1967
SOV/11-10-14/11

Ion exchange resins KU-2 and ENE-10 were used in the experiments. There are 10 references. U.S., 1 German, 1 Soviet. Three U.S. references are: M. Gibbs, J. Am. Chem. Soc., 79, 700 (1957); J. Sowden, Adv. Carboh. Chem., 12, 79 (1957).

ASSOCIATION: Leningrad Technological Institute and Institute of High-Molecular Compounds, Academy of Sciences USSR (Leningradskiy tekhnologicheskii institut imeni Leningra I Institut vysokomolekulyarnykh soedineniy Akademii nauk SSSR)

SUBMITTED: January 14, 1967

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